

# **STANDARD METHODS OF CHEMICAL ANALYSIS**

The first four editions of **STANDARD METHODS OF CHEMICAL ANALYSIS** were prepared under the Editorship of Dr Wilfred W. Scott, Professor of Chemistry at the University of Southern California. After his death, the Fifth Edition was edited by Dr N. Howell Furman, then Professor of Chemistry at Princeton University. Professor Furman also edited Volume I of the Sixth Edition and is Advisory Editor of Volume II, which is edited by Dr Frank J. Welcher of Indiana University. Volume III will be devoted entirely to instrumental methods.



# STANDARD METHODS OF CHEMICAL ANALYSIS

SIXTH EDITION

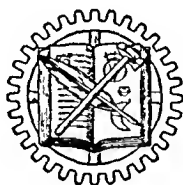
*Volume Two—Industrial and Natural Products and  
Noninstrumental Methods*

Part B

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## Chapter 32

# EXPLOSIVES AND PROPELLANTS\*

By Raymond H. Pierson

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Explosives are chemical compounds or mixtures of chemical compounds that release energy when burned or detonated. They are distinguishable from fuels used in furnaces or heat engines in that they do not, in general, require air for their combustion; they contain their own oxidant. Their purposes, performance characteristics, and compositions extend over wide ranges. Sometimes great heat or light is desired; sometimes heat or light may be incidental and relatively unimportant; sometimes holding heat, light, or both, at minimum levels, is desired. In many blasting or propelling applications, for example, only the work from expanding gases produced by combustion is of primary importance, while for a flare, only the production of light is essential.

Propellants are sometimes thought of as "low explosives," thus reserving the term "explosives" to mean "high explosives." This distinction has its basis largely in function rather than in type of material. Furthermore, behavior of a given material depends on a variety of circumstances. Many materials will explode (detonate) if confined, but burn quietly (although rapidly) if unconfined. Some, which detonate if ignited by a blow (impact), will burn quietly if ignited by a flame. Black powder is used as a bursting charge in mining or in firecrackers, but burns more slowly and without detonation in fuzes and igniters. Nitroglycerin, at the 40% level, detonates in dynamites, but burns without detonation at the 40% level in a rocket propellant, or at the 20% level in a cannon propellant. The terms "high explosive" and "low explosive" have little significance in the discussion of methods for the analysis of explosive materials.

No attempt is made in this chapter to differentiate between commercial and military products because of the extent of overlap between these two fields. Many products are used for both commercial and military purposes. Large stores of TNT were on hand at the end of both World War I and World War II, and were used subsequently in commercial work. Detonating and priming compositions are used in conjunction with both commercial and military applications of explosives, propellants, and pyrotechnics.

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# ***BLACK POWDER***

Black powder is the oldest explosive, propellant, or pyrotechnic. It is given first place in this chapter chiefly because of its historical interest. It still has diversified uses, although the quantities produced have been steadily and rapidly decreasing during recent decades. Commercial use in the United States was 33000 tons in 1939, 10000 tons in 1949, and only 1000 tons in 1959. Currently, black powder comprises less than 3% of total production of explosives in the United States.

## **SAMPLING**

From 50 to 100 g. of the original sample are crushed in small portions in a porcelain mortar, and completely passed through an 80-mesh sieve, care being taken to avoid undue exposure to the air. The separate powdered portions are promptly bottled and finally, the entire sample is well mixed.

Throughout the crushing operation, the main portions of the uncrushed and crushed powder are kept at a safe distance from the spot where crushing is being done, so that in the event of ignition of the small increment being crushed, the larger portions of the powder will not be ignited.

## **MOISTURE**

Moisture is determined by desiccation of a 2-g. sample for 3 days over indicating Drierite.

## **NITRATES**

Nitrates are determined gravimetrically by extraction of a weighed sample with warm distilled water using a Gooch crucible with a thick asbestos pad. If barium nitrate is present, a gravimetric determination of barium as the sulfate is made.

## **SULFUR**

Sulfur is determined by a  $\text{CS}_2$  extraction of the residue in the Gooch crucible from the nitrate determination, and reweighing of the dried crucible.

## **CHARCOAL**

The residue in the crucible from the sulfur determination is considered to be charcoal and ash.

## **ASH**

Ash is determined as the residue upon ignition of the charcoal.

# GENERAL METHODS

In order to avoid frequent repetition a number of procedures that are common to the systematic analysis of several explosive compositions or to the ingredients used in the manufacture of explosives or propellants are presented in this section. Additional specific instructions or modifications are indicated in other sections wherever necessary.

A few of the more important thermodynamic and stability tests are presented here; many other such tests cannot be included for reasons of space. The great number of physical tests that are usually conducted in the chemical laboratory or in close conjunction with it are also omitted. For example, tests for particle size and particle size distribution are not included here although these tests are of great importance in many cases and appear in numerous specifications for ingredients. Ballistic tests and sensitivity tests (impact, friction, autoignition by heat and ignition by electrostatic discharge, etc.) are considered to be outside the scope of this chapter. The details of many of these omitted tests and the principles involved may be found in standard works on explosives<sup>1, 3, 4</sup> and in military specifications and standards.\*

## HEAT OF EXPLOSION\*

The sample is burned in an oxygen-type bomb under an atmosphere of nitrogen or helium. The preferred equipment is as follows: (1) adiabatic calorimeter Parr Series 1200 (Parr Instrument Company, Moline, Ill.) with Series 1100 bomb, Series 1500 water heater, and two narrow range matched thermometers having 0.02°C graduations; Series 1600 with certificates; or (2) plain jacket calorimeter Series 1300 with Series 1101 bomb and narrow range or differential thermometers having 0.01°C divisions calibrated against a Bureau of Standards certified standard thermometer.

The following Parr items (or their equivalent) are recommended: oversize cup 3102, fuse wire 45C10, reading lens 3003, and ignition equipment 2900. Parr Manual No. 120, *Oxygen Bomb Calorimetry and Oxygen Bomb Combustion Methods* is an appropriate reference.

**Procedure**—Determine the water equivalent of the calorimeter by burning high purity benzoic acid (Parr or National Bureau of Standards) in oxygen using a loading density (grams sample per cubic centimeter of bomb capacity) of  $0.0027 \pm 0.0005$  g per cubic centimeter and an oxygen pressure of  $25 \pm 1$  atm. As the sample cup used in calibrating must be different from the one used for heat of explosion determinations, correct the determined water equivalent for this dif-

Davis, Tenney L. *The Chemistry of Powder and Explosives*. John Wiley and Sons, Inc., New York, 1945.

\* Military Standard 286, *Propellants Sampling Inspection and Testing*, June 1956. Obtainable from the Superintendent of Documents, U. S. Government Printing Office, Washington 25, D. C.

<sup>3</sup> Based on *Standard Methods and Procedures for the Determination of Heat of Explosion of Rocket Propellant Powders*, NavOrd OD 9310, a Navy Department Bureau of Ordnance publication, June 1953.

ference, or use an auxiliary piece of metal (same type as the cup), of appropriate weight, in the bottom of the bomb during the calibration runs. If helium is used for the heat-of-explosion determinations, correct the water equivalent for the heat capacity difference between oxygen and helium. This difference amounts to 0.7 cal. per degree C. when both gases are used at 25 atm. pressure. No correction is necessary if nitrogen is used.

**Procedure with the Adiabatic Calorimeter.**—Use a loading density of  $0.0150 \pm 0.0005$  g. per cubic centimeter, and weigh the sample to the nearest 0.1 mg. Follow the techniques of Parr Manual No. 120. Tie the fuse wire so that the length between electrodes is the same for each determination. Flush the bomb twice by filling with inert gas to 25 atm. and releasing it to the atmosphere. Then fill the bomb a third time to  $25 \pm 1$  atm. Adjust the temperature of the water in the calorimeter bucket to a temperature that is below room temperature by one half the amount of expected temperature rise, and weigh the bucket and water. Assemble the calorimeter and adjust the temperature of the circulating water to match that of the water in the bucket. Operate the calorimeter for 5 min., adjusting the jacket water to attain equilibrium, and record the bucket water temperature at 1-min. intervals until at least 4 readings have been made (tap the thermometers gently to prevent false readings). When the readings are constant, fire the charge by closing the ignition switch, then releasing it when the pilot light ceases to glow. Follow the temperature rise of the bucket water by adding hot water to the jacket. After the initial rapid rise of about 3 min. duration, maintain the jacket temperature as close as possible to that of the bucket water. When the temperature rise is nearly ended (about 6 min.), record the bucket water temperature at 1-min. intervals until 4 successive readings show no additional rise. Record the maximum (final) temperature. Release the gas from the bomb into a hood.

**Calculations for Adiabatic Procedure.**—Correct the observed initial and final temperature reading by referring to the thermometer calibration chart. The corrected temperature rise is the difference between the two corrected readings. Heat liberated equals water equivalent times corrected temperature rise. (Make no correction for fuse wire or acid production.)

$$\text{Heat of explosion in calories per gram} = \frac{\text{heat liberated}}{\text{grams sample}}$$

**Procedure for the Plain-Jacket Calorimeter (Isothermal).**—Use a loading density of  $0.015 \pm 0.005$  g. per cubic centimeter, and weigh the sample to the nearest 0.1 mg. Follow the techniques of Parr Manual No. 120. Tie the fuse wire, flush the bomb with inert gas, and adjust the temperature of the water in the bucket, in the manner described for adiabatic operations. Weigh the bucket and its water, and assemble the calorimeter. Operate the calorimeter for at least 3 min. before beginning to record thermometer readings. Then record thermometer readings at 50-sec. intervals for 12 intervals (10 min.). The rate of heat gain is determined from the readings of the last 5 min. of the period (provided the rise is uniform; if it is not, repeat the preliminary readings for determination of steady heat rise). At the end of the initial period, record the exact calorimeter temperature (to  $0.001^\circ\text{C}.$ ) and fire the charge, releasing the switch as soon as the pilot light ceases to glow. Record also the time at the instant of firing (corresponding to the initial temperature). After 50 sec., record the temperature to the nearest  $0.01^\circ\text{C}.$  and at each 10-sec. interval for a period of 50 sec. Then continue to take readings

Percentage of hygroscopicity of the propellant equals the sum of the percentages for the two specimens.

### CANNON PROPELLANTS

**Procedure.**—Weigh two 100-g. portions of the propellant sample into tared weighing bottles with ground glass covers. Place each sample, minus the glass cover, in a 10-l. capacity desiccator containing 90% humidity-producing solution ( $18.6 \pm 0.5\%$  w/w sulfuric acid). Place the desiccator in an oven maintained at  $30^\circ \pm 2^\circ\text{C}$ . After 4 days remove the bottles from the oven, cover each with its glass cover, cool to room temperature in a desiccator containing indicating desiccant, and reweigh. Repeat the oven-humidity treatment and reweighing daily until the change of weight of each bottle on successive weighings is not greater than 0.2 mg.

Determine the moisture content of the sample *as received* by the method of oven drying at  $100^\circ\text{C}$ . as described under "Moisture and Volatiles, by Oven Drying at  $100^\circ\text{C}$ ," p. 1294.

$$\text{Percentage of hygroscopic moisture of the propellant} = A + B$$

where  $A$  = average percentage increase in weight of the 2 specimens subjected to the 90% humidity at  $30^\circ\text{C}$ ., and

$B$  = percentage of moisture in the propellant as received.

### MOISTURE BY THE CARBON TETRACHLORIDE DISTILLATION PROCEDURE

Several types of distillation traps have been used for the determination of water by distillation with carbon tetrachloride. Of these, one corresponds to an apparatus used by the Hercules Powder Co., and another to that used by the E. I. DuPont de Nemours and Co. The Hercules type has a 6.0-ml. graduated portion; the DuPont type has a 1.0-ml. graduated portion. Figure 32-1 shows the 6.0-ml. tube, and Fig. 32-2 shows an assembly with the 1.0-ml. tube and an enlarged view of the tube. A suitable bath may be made by modifying either item No. 9864 or No. 9865 of the Arthur H. Thomas Co., in order to maintain the water level at about the half-full position.

For propellants or dynamites containing not more than 40% nitroglycerin, use a 100-g. sample for the 6.0-ml. trap, and a 50-g. sample for the 1.0-ml. trap. For samples of more than 40% nitroglycerin, reduce the sample size one-half. In case the sample contains a large amount of water, reduce the amount of sample taken in an appropriate manner.

**Procedure.**—Place the specimen in a dry 500-ml. balloon flask and add 200 ml. of dry  $\text{CCl}_4$ . Insert a plug of cotton in the top of the condenser and then connect a small drying tube to prevent access of atmospheric moisture. Reflux on a steam or hot water bath for the appropriate length of time as described for specific materials (see "Procedure D-1, Moisture by Carbon Tetrachloride Distillation," p. 1353, and "Moisture by Carbon Tetrachloride Distillation," p. 1374). The reflux should be at a rate which causes distillate to fall from the tip of the condenser at 2 or 3 drops per sec.

Read the point of contact of the top meniscus with the wall of the tube and

read the highest point of the lower meniscus. Record the difference in readings as volume of water and calculate percentage by weight of water considering 1 ml of water equal to 1 g.

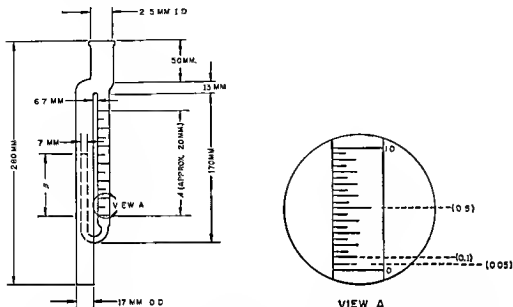


FIG. 32.1. Water by Distillation Tube (6 ml Type). Capacity of Graduated Portion 60 ml. Smallest Intervals 0.05 ml. Numbered at Each 10 ml Division. Length *A* Must Be 1.6 Times as Long as *B*.

## MOISTURE BY KARL FISCHER TITRATION

The Karl Fischer titration is applied to many of the ingredients used in manufacturing explosives or propellants and occasionally to the manufactured products. Metal oxides, oxidizing or reducing agents, carbonyl compounds, and many amines interfere unless special techniques are used to eliminate the interferences. Moisture in nitrocellulose base propellants is usually determined by the desiccation method or carbon tetrachloride distillation rather than the Karl Fischer titration because of sampling problems encountered in the latter case. Some nitrocellulose base propellants can be handled directly in the Karl Fischer titration vessel using methanol or propylene oxide-methanol (2:1) as solvent, but usually a separate vessel and extraction procedure is desirable or necessary. Of these external extraction methods, the simplest involves the use of a glass-stoppered conical flask and a shaking machine. The sample is shaken with solvent for a period of 30 min. to several hours, depending on the formulation, and an aliquot is taken for titration. For samples containing nitrocellulose of about 12.2% nitrogen and higher, methanol is a satisfactory solvent. But methanol has too much solvent power when used with nitrocellulose material of lower than 12.2% nitrogen content and as a consequence produces highly viscous solutions or gummy mixtures. Isopropanol or a mixture of isopropanol and methanol is advantageous for the extraction of materials containing nitrocellulose of the lower nitrogen content. In other spe-

cial cases ethylene glycol, ethylene glycol-pyridine, or methanol-pyridine mixtures may be used as solvents for the samples.

The following details are recommended for work with explosive or propellant materials.

**Apparatus.**—Two automatic 25-ml. or 10-ml. burets, one for Karl Fischer (K.F.) reagent and one for water-in-methanol solution, are arranged to dispense into a

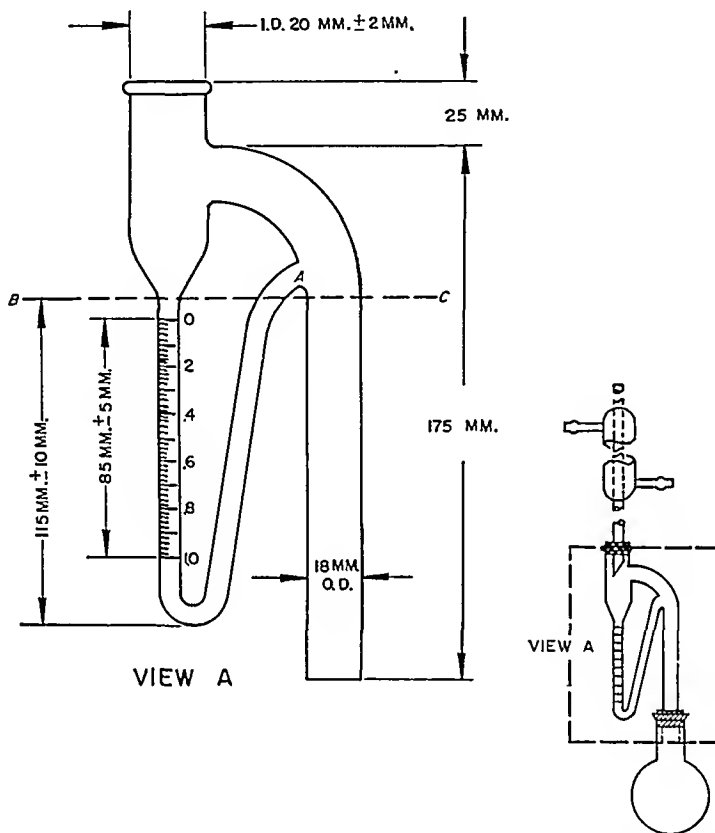


FIG. 32-2. Water by Distillation Tube (1-ml. Type) and Assembly: Capacity of Graduated Portion, 1.0 ml.; Smallest Intervals, 0.02 ml.; Numbered at 0.2-ml. Lines; Overflow Point, A, Must Be at Least 5 mm. Above Line B-C.

titration cell (tall-form beaker or jar) equipped with a cover that is gas tight or nearly so. This cover has openings for extended buret tips, electrodes, dry-gas inlet, and sample-inlet plug. Teflon is a suitable material for the cover and the sample-inlet plug. The sample-inlet opening is about 1 in. in diameter. When assembled, all the openings in the lid are tightly sealed to protect the cell from atmospheric moisture. Oil-pumped cylinder nitrogen is dried by passage through a 3 ft. tube about 1 in. in diameter, containing Drierite or magnesium perchlorate, followed by a 1-ft. tube containing phosphorus pentoxide or Linde molecular sieve No. 4A. The dry nitrogen is supplied to the titration cell, the burets, and the storage bottles for the K.F. and water-in-methanol reagents. When not in use,



after converting the weight of sodium tartrate dihydrate used to milligrams of water. The dihydrate normally contains 15.66% water by weight. This value can be checked by obtaining the loss in weight of a sample of the dihydrate heated in an oven at 150°C. to constant weight (about 3 hr.).

Some activities find it advantageous to use a secondary, strong K.F. solution for equilibrating solvents in the titration cell before the introduction of samples. Only approximate standardization against the water-in-methanol solution is needed for this titrant.

*Procedure for Solid and Liquid Samples.*—Ideally, use a sample which contains 30 to 60 mg. of water. For solids, transfer the approximate amount desired to a dry weighing bottle and obtain the gross weight. Transfer to the titration cell sufficient dry methanol (or other solvent) to dissolve the sample and to cover the electrodes. Consume the water in the solvent with K.F. reagent, obtaining equilibration (end point). Transfer most of the solid sample from the weighing bottle to the titration cell and restopper the nearly empty bottle. Keep the time of exposure of the sample to the atmosphere at a minimum. Close the titration cell, stir until the sample is all or nearly all in solution, and complete the determination as described for the dihydrate standardization. Then reweigh the nearly empty weighing bottle.

$$\text{Percentage of water} = \frac{0.1E(A - rB)}{W_1 - W_2}$$

where  $E$  = water equivalent of K.F. reagent, in milligrams per milliliter,

$A$  = total volume of K.F. solution added to the cell after introduction of the sample, in milliliters,

$B$  = volume of water-in-methanol solution used in back-titration, in milliliters,

$r$  = ratio, K.F. per water-in-methanol,

$W_1$  = gross weight of weighing bottle and sample, in grams, and

$W_2$  = weight of nearly empty weighing bottle, in grams.

Liquid samples are titrated in the same way as solid samples, but sample introduction to the cell may be by weight from a Lunge pipet or by volume from a pipet, and the amount of auxiliary solvent required may be less.

For a direct titration with K.F. reagent alone, the calculation becomes

$$\text{Percentage of water} = \frac{0.1EA}{W_1 - W_2}$$

If a sample is made up in a solvent and an aliquot is taken, a correction is applied for the amount of water in the solvent of the aliquot.

$$\text{Percentage of water} = \frac{0.1E(A - S)}{W}$$

where  $S$  = milliliters of K.F. reagent for the solvent,

$W$  = grams of sample in the aliquot, and  $E$  and  $A$  are as above.

For many materials, the titration may be made directly with K.F. reagent to an end point on addition of the reagent, rather than by back-titration of excess with the water-in-methanol solution. Certain commercial equipment that automatically determines the end point is especially convenient for the direct titration.

### MOISTURE AND VOLATILES BY OVEN DRYING AT 100°C

The 100 C oven procedure is a general method applicable to many ingredients triple base propellants double base propellants containing less than 20% nitro glycerin and ball propellants (for external moisture on the latter) Propellants should be whole or cut grains but *not* ground samples

**Procedure**—Four to 5 g of sample are weighed in a tared preconditioned 25 ml Erlenmeyer flask (with ground glass stopper) The flask should have a 40 mm base diameter 60 mm height and 15 mm neck opening The assembly is heated unstoppered for 2 hr at  $100^{\circ} \pm 2^{\circ} \text{C}$  in an oven at atmospheric pressure It is then cooled in a desiccator for at least 30 min At the end of this time the flask is re stoppered and reweighed The loss in weight is calculated to percentage of moisture and volatiles

**Caution** Special ovens are required and overheating must be avoided

### MOISTURE AND VOLATILES BY VACUUM OVEN DRYING AT 55°C

The determination of volatiles by vacuum oven is at times required for single base propellants and for heat sensitive materials

**Procedure**—A 10 g sample is placed in a tared preconditioned aluminum or glass weighing dish having 60 mm diameter and a 30 mm depth The assembly is heated for 6 hr in a vacuum oven maintained at  $55^{\circ} \pm 2^{\circ} \text{C}$  and an absolute pressure of  $80 \pm 10$  mm of mercury (a pressure regulating device is required in connection with a vacuum system) The dish and sample are cooled in a desiccator and reweighed Percentage of moisture and volatiles is calculated from the loss of weight during heating

### NONAQUEOUS TITRATION

Nonaqueous titration has been applied to the analysis of a variety of explosive materials Details of the procedure as utilized for the determination of potassium nitrate and of potassium sulfate are presented in the section on nitrocellulose base solid propellants under Potassium Nitrate by Nonaqueous Titration p 1398 and Potassium Sulfate by Nonaqueous Titration p 1399 The detailed procedure for the determination of ammonium nitrate is given in the section on composite propellants under Ammonium Nitrate by Nonaqueous Titration p 1406

Table 32 I is based on an article by Sarson<sup>10</sup> and shows some of the explosive compositions to which the nonaqueous method has been advantageously applied Inorganic nitrates are separated from organic nitro and nitrate compounds by extraction of the organic materials with hot methyl isobutyl ketone Ammonium nitrate is determined by a colorimetric titration in dimethylformamide total inorganic nitrates by a colorimetric titration in acetic acid For these titrations of inorganic nitrates a standard solution of perchloric acid in dioxane is used Tri nitrotoluene (TNT) dinitrotoluene (DNT) cyclotrimethylenetrinitramine (RDX) and pentaerythritol tetranitrate (PETN) are titrated potentiometrically in methyl isobutyl ketone using a standard solution of tetrabutyl ammonium hydroxide in

<sup>10</sup> Sarson R D Anal Chem 30, 932 1958

TABLE 32-1. SOME COMPOSITIONS AMENABLE TO ANALYSIS BY NONAQUEOUS TITRATION  
*Per Cent by Weight of Various Ingredients*

$\text{NH}_4\text{NO}_3$	$\text{NaNO}_3$	TNT	DNT	NG	RDX	PETN
70	20	10				
70	20		10			
50	20	15	15			
70	10			20		
60	20				20	
70	10					20

methanol or benzene. Nitroglycerin is determined by evaporating off the methyl isobutyl ketone used as separating solvent, taking up the nitroglycerin (NG) in dimethylformamide and titrating potentiometrically using standard tetrabutyl ammonium hydroxide solution.

### STABILITY BY INTERNATIONAL TEST AT 75°C.

*Procedure.*—A 10-g. sample of the explosive is placed in a tared weighing bottle 35 mm. in diameter and 50 mm. deep, on top of which is placed a watch glass. The bottle and contents are heated at 75°C. for 48 hr., cooled, weighed, and examined for fumes or decomposition as indicated by appearance or odor. If the loss in weight exceeds any moisture present in the sample, as determined by drying in a desiccator, volatility or decomposition is indicated. This test is applicable to commercial blasting, as well as military explosives, and is significant only when the material is volatile or unduly unstable. It is of interest chiefly as a preliminary test for new explosives.

### STABILITY BY POTASSIUM IODIDE-STARCH TEST

For stability by the potassium iodide-starch test, see the description given under "Stability Test: Heat Test with Potassium Iodide-Starch Paper," p. 1333.

### STABILITY BY HEAT TEST AT 120° OR 134.5°C. WITH STANDARD METHYL VIOLET TEST PAPER

The stability test with standard methyl violet test paper is applied to nitrocellulose and to propellants. The test at 134.5°C. for nitrocellulose is described in detail under "Stability Test at 134.5°C. Using Methyl Violet Paper," p. 1334. When applied to propellants, the following changes from the procedure for nitrocellulose may be made (as required by applicable specifications): (1) tests may be required at 120°C. or at 134.5°C. or at both temperatures; (2) 5 replicate specimens are run (the color test is considered complete when any tube has changed color completely); (3) after completion of the test for color change, the test, when made

Adjust the total volume of the heating tube and the helix (up to the fiducial mark) to exactly 6 ml., by placing an appropriate number of 3-mm. glass beads in the heating tube.

NOTE.—The average volume of the beads in a lot can be calculated by placing 100 beads, 10 at a time, in a buret partially filled with distilled water, noting the water displacement, and dividing by 100. The uniformity of the lot may be checked by noting the displacement of each set of 10 beads.

Reconnect the helix to the apparatus.

*Procedure.*—Make duplicate determinations. Prepare the propellant specimen by grinding or rasping so that its particles are in the range 10- to 40-mesh in size.

Transfer a  $1.000 \pm 0.001$ -g. specimen to the heating tube, connect the tube to the helix, and heat the tube in the heating block at  $110^\circ \pm 0.1^\circ\text{C}$ .

Adjust the 3-way stopcock, *H*, in the connecting tube so that the helix and heating tube are connected to the nitrogen supply and vacuum pump *L*.

Evacuate the tube and helix to a pressure of 5 mm. mercury. Then allow nitrogen to enter the tube and helix at such a rate that bubbles will form in the bubble counter too rapidly to be counted but slow enough so that they will not vigorously agitate the liquid.

Repeat the evacuation and nitrogen purging 4 times more. At the end of the fifth purge, adjust the stopcock, *H*, to seal the helix and heating tube. Disconnect the nitrogen-evacuation system. (The nitrogen in the system should be at approximately atmospheric pressure.)

Allow the tube and helix to remain sealed for 15 min. while continuing the heating.

At the end of 15 min., release the pressure from the helix by opening the stopcock, *H*, and quickly closing it again.

With the stopcock turned so that the helix is sealed and the manometer is open to atmosphere, raise the level of the mercury until the stopcock is full of mercury. Then turn the stopcock to close the system to atmosphere and open the manometer to the helix. With the stopcock in this position, adjust the mercury-leveling device until the mercury rises to the fiducial mark. Note the reading on the manometer. (This reading is the zero reference point from which all further readings are measured.) Also record the barometer reading.

After 30 min., readjust the mercury level to the fiducial mark and record the corresponding manometer reading. Also record the barometer reading.

Determine the absolute pressure of the system by adding any changes in barometric pressure to the new manometer reading, and subtracting the zero reference reading.

Repeat the readjustment of the mercury level and record the manometer reading every 30 min. until the mercury has risen 150 mm. above the zero reference point.

NOTE.—The absolute pressure for duplicate tubes of a propellant lot should agree within 4 mm. in the 0- to 50-mm. range, within 6 mm. in the 50- to 100-mm. range, and within 8 mm. above 100 mm.

Average the readings for the 2 specimens.

Prepare a graph on linear paper, with time in minutes on the abscissa and the average absolute pressure on the ordinate.

Report the slope at 100 mm. and at 100 min., and report the time to 100 mm.

### STABILITY BY VACUUM STABILITY TEST (FOR PROPELLANTS OR INGREDIENTS)

The vacuum stability test is usually made at 90°C for double base propellants at 100°C for single base propellants and at 120° for certain ingredients such as

penterythritol tetranitrate. It has occasionally been used at other temperatures for example 150°C. One to 5 g samples are used depending on the type of material and the specifications applicable.

**Apparatus**—The glass assembly of the apparatus is illustrated in Fig 32.4. Constant temperature ( $\pm 0.5^\circ\text{C}$ ) is maintained by a reflux bath using mixtures of ethinol and water, glycerin and water or toluene and xylene.

**Standardization of the Apparatus**—Determine the volume of the heating tube by filling it with mercury from a buret until the mercury reaches the level at which it will contact the ground glass joint of the capillary tube. Determine the unit capacity of the capillary by placing exactly 10 g of mercury in its cup and manipulating the tube so that all the mercury passes into the long (85 cm) section of the capillary. Be sure that the mercury remains as a continuous

column. Measure the length of the mercury column at 3 positions in the long section of the capillary and average the 3 measurements. Calculate the unit capacity of the capillary using the following formula:

$$B = \frac{W}{13.59 L}$$

where  $B$  = unit capacity of capillary in milliliters per millimeter,

$W$  = weight of mercury in grams and

$L$  = average length of mercury column in millimeters

**Procedure for Propellants**—Solventless propellants can be tested without drying but solvent propellants should be dried for 4 hr at 100°C before testing. By grinding (Wiley mill) or rasping prepare a sample of about 12 mesh particles. Place a 5.00 g specimen in the heating tube.

Coat the ground glass joint of the capillary tube with a light film of petroleum jelly, and make an airtight connection between the heating tube and the capillary by pressing the tube up against the capillary with a twisting motion.

Mount the apparatus on a rack so that the long section of the capillary is nearly vertical and the cup at the bottom rests on a solid support.

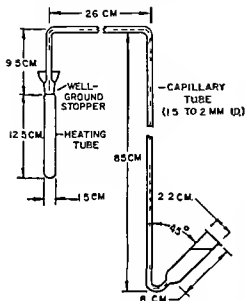


FIG 32.4 Vacuum Stability Test Glass Assembly

Fill the cup with 7.0 ml. of mercury, and connect a vacuum line to the mouth of the cup. Evacuate the capillary to a pressure of approximately 5 mm. of mercury (absolute). (Evacuation is facilitated by tilting the apparatus until the capillary opening in the bottom of the cup is free from mercury.)

When the pressure has been reduced to 5 mm. of mercury, remove the vacuum source and allow the mercury to enter the capillary. Record the following data: (1) length of capillary from heating tube joint to surface of mercury pool in cup ( $C_1$ ); (2) height of mercury column above the surface of the mercury pool ( $H_1$ ); (3) barometric pressure in millimeters of mercury ( $P_1$ ); and (4) temperature of room in degrees Centigrade ( $t_1$ ).

Immerse the heating tube in the constant-temperature bath, being careful not to loosen the connection between the heating tube and the capillary. Heat the tube for 40 hr.

Remove the tube from the constant-temperature bath, and allow it to cool to room temperature.

Record the following data: (1) length of capillary from the heating tube joint to the surface of the mercury pool in the cup ( $C$ ); (2) height of mercury column above the surface of the mercury pool ( $H$ ); (3) barometric pressure in millimeters of mercury ( $P$ ); (4) temperature of the room in degrees Centigrade ( $t$ ).

Calculation.—Calculate the volume of gas (at standard temperature and pressure) liberated during the test as follows:

$$\text{Volume of gas in milliliters} = (A + BC) \frac{273(P - H)}{760(273 + t)} - (A + BC_1) \frac{273(P_1 - H_1)}{760(273 + t_1)}$$

where  $A$  = volume of heating tube in milliliters, minus 5 ml. (allowance for specimen),

$B$  = unit capacity of capillary in milliliters per millimeter,

$C$  = length of capillary from heating-tube joint to top of mercury column at *end* of test in millimeters,

$C_1$  = length of capillary from heating-tube joint to top of mercury column at *beginning* of test in millimeters,

$H$  = height of mercury column above surface of mercury pool at *end* of test in millimeters,

$H_1$  = height of mercury column above surface of mercury pool at *beginning* of test in millimeters,

$P$  = atmospheric pressure at *end* of test in millimeters,

$P_1$  = atmospheric pressure at *beginning* of test in millimeters,

$t$  = temperature of room at *end* of test, and

$t_1$  = temperature of room at *beginning* of test.

## STRAND BURNING RATE OF SOLID ROCKET PROPELLANTS

Detailed instructions for determining the strand burning rate of solid rocket propellants are given in the Navy Department Bureau of Ordnance publication NavOrd OD 9376.<sup>12</sup> The following directions are based on this reference. Information concerning the availability of sketches referred to in the original publication may be obtained from the Bureau of Naval Weapons, Navy Department,

<sup>12</sup> Standard Methods and Procedures for the Strand Burning Rate Evaluation of Rocket Propellant Powders, NavOrd OD 9376, May, 1953.

graduated into 5-p.s.i. intervals (e.g., Heise-Bourdon gauge No. 2430, Heise Bourdon Tube Co., Inc.).

**Electric Timing Clocks.**—Clocks must be suitable for recording time to at least 60 sec., and graduated to 0.01 sec. (e.g., Precision timer Model S-1, 115 volt AC, 60 cycle, 6 volt DC clutch, 2 hands, 1 r.p.m. and 1 r.p.s., Electric Time Co., Inc.).

**Electric Circuits.**—These must be available for controlling the timing clocks.

**High Pressure System, Valves, Tubing, etc.**—See Fig. 32-7.

**Materials. Nitrogen Gas (Cylinders).**—Cylinders should contain not more than 0.10% oxygen.

**Polyvinyl Chloride-Acetate Copolymer.**—Bakelite VYLF, as produced by Carbide and Carbon Chemicals Div., Union Carbide and Carbon Corp., or the equivalent.

**Liquid Plasticizer.**—Flexol R-2H, as produced by Carbide and Carbon Chemicals Div., Union Carbide and Carbon Corp., or the equivalent.

**Methylene Chloride, Technical Grade**

**Polyvinyl Alcohol.**—Elvanol 90-25, as produced by E. I. DuPont de Nemours and Co., or the equivalent.

**Glycerin, Reagent Grade.**

**Aersol OT (100%), or Equivalent.**

**Alumel or Chromel Wire.**—No. 26 gauge (Brown and Sharpe), or the equivalent.

**Fuse Wire, 0.5 to 1.0 Ampere.**

**Strand Inhibitor Solutions.** Polyvinyl Chloride-Acetate Solution (PVCA). *Composition (Weight Per Cent):*

12.0% polyvinyl chloride-acetate copolymer.

1.5% plasticizer.

86.5% methylene chloride.

**Preparation.**—Add plasticizer to the methylene chloride; then add the polyvinyl chloride-acetate copolymer slowly with constant agitation. The resultant solution should be clear and free of air bubbles. The viscosity of the solution is held substantially constant by dilution as necessary with methylene chloride.

**Polyvinyl Alcohol Solution (PVA).** *Composition (Weight Per Cent):*

5.0% polyvinyl alcohol.

0.2% Aerosol OT.

10.0% glycerin.

84.8% water (distilled).

**Preparation.**—Make up about a 10% solution of Aerosol OT in water. Add Aerosol solution and glycerin to the water and cool to  $15^{\circ} \pm 5^{\circ}\text{C}$ . Add the polyvinyl alcohol slowly with constant agitation until evenly dispersed. Raise the temperature slowly to  $80^{\circ}\text{C}$ . while stirring, and continue to heat until all polyvinyl alcohol has gone into solution. Cool to room temperature before using.



FIG. 32 6. Strand Burning Rate Apparatus, Strand Holder with a Strand in Place. (Official United States Navy Photograph.)

hole at least  $\frac{1}{4}$  in. from the igniter wire. The number of holes corresponds to the number of fuse wires to be used. This number is dependent upon the number of independent electrical circuits available in the strand burning-rate apparatus. It is desirable to use 4 fuse wires. The distance between adjacent holes should be accurately known (within  $\pm 0.01$  in.).

The best method for accomplishing this step is to use a drilling jig that will hold the strand firmly, and will indicate accurately the point at which the hole is to be drilled. After drilling, add the clock-starting and stopping fuse wires (0.5- or 1.0-amp. fuse wire depending upon clock control circuits). Apply a final coat of PVA solution and dry for 15 to 20 hr. at  $100^{\circ} \pm 5^{\circ}\text{F.}$  before burning. (After the final coat is applied, the fuse wires should be straightened to be perpendicular to the strands, to prevent the wires from drying under the inhibitor and damaging the coating.) The drying oven should be in an air conditioned room held to the same limits of temperature and humidity as specified for the inhibiting operation. To ensure maintenance of low humidity of the air, the oven should have a forced circulation and by-pass system for partial exchange of air.

Alternatively, the following procedure may be used: apply a third coat of PVA solution, and dry in the open air for a minimum of 60 min.; dry the strands in a laboratory oven according to the procedure indicated above, and then drill and wire the strands.

NOTE.—The inhibiting materials and procedures described above are typical, but other materials or procedures may be required for some types of propellants.

**Test Procedure.**—Follow the specific requirements of the applicable specifications regarding: number of strands to be burned; inhibiting procedure; pressures of burning; and temperature of burning.

Make sure the bath regulation is within the  $\pm 2^{\circ}\text{F.}$  for the specific temperature.

Attach the ignition and fuse wires for the strand to the appropriate terminals in the strand holder. Attach the holder and closure assembly, check the electrical circuitry, and screw the holder assembly into the burning-rate apparatus. Pressurize the chamber and surge tank with nitrogen to the desired pressure ( $\pm 30$  p.s.i.).

Condition the strands in the apparatus for not less than 7 min. at the required test pressure.

Reset the clocks to zero, make sure the pressure is adjusted at the required level, and fire the strand by closing the firing switch momentarily until a slight jump in pressure indicates that the strand is burning. Record the starting pressure, maximum pressure attained during burning, the average pressure, and the atmospheric pressure.

Record the clock readings to the nearest 0.005 sec. (or closer if greater accuracy is possible).

Close the valve connecting the surge tank and the burning chamber (to conserve nitrogen), exhaust the burning chamber, and remove the strand holder. Carefully clean the chamber and holder, removing all residue.

**Computation.**—Calculate to the nearest 0.001 in. per sec., the average burning rate,  $r_0$ , of each strand, and the average of replicate strands for a specified temperature and pressure. Plot on log-log paper the burning-rate curves for each temperature, plotting rate vs. pressure. Detailed computation procedures for each rocket propellant are provided in the applicable specifications. These instructions include criteria for the rejection of values of individual burning rates of in-



When a blank is unnecessary, the above equation simplifies to

$$\text{Percentage of ingredient} = \frac{(f)NV}{W} \quad \text{Eq. 32-2}$$

**For a Back-Titration. Case 1, Calculation Based on One Normality.**

$$\text{Percentage (of ingredient sought)} = \frac{(\text{factor}) N(B - A)}{W} \quad \text{Eq. 32-3}$$

where *factor*, *N*, and *W* are as above, but *B* = milliliters of standard titrant (of normality *N*) used in back-titration of a specific amount of added reactant(s) when no sample is present, and *A* = milliliters of the same standard titrant required for the back-titration when a sample is present.

Hence, (*B* - *A*) is a measure of the reagent(s) consumed by the sample in terms of the back-titrant.

**For a Back-Titration. Case 2, Calculation Based on Two Normalities.**

$$\text{Percentage (of ingredient sought)} = \frac{(\text{factor})(AN - BN')}{W} \quad \text{Eq. 32-4}$$

where *factor* and *W* are as before, but

*A* = milliliters of a first standard titrant added in excess,

*N* = normality of titrant *A*,

*B* = milliliters of a second standard titrant used in back-titration, and

*N'* = normality of the titrant used in back-titration.

# INGREDIENTS

This section on ingredients presents analytical procedures for only a few of the many hundreds of ingredients used in manufacturing explosives and propellants. A partial list of the more important military specifications is given in Appendix A, following this chapter.

## ALUMINUM

Powdered aluminum, of a wide variety of particle sizes, in flaked, grained, or atomized form, is used to a considerable extent in explosives, propellants, and pyrotechnics.

### ASSAY OF METALLIC ALUMINUM BY WATER CONVERSION

**Procedure**—A 1 g sample contained in a small glass capsule is treated in a decomposition flask with 30 ml of 20% NaOH solution. The generated hydrogen is swept by a stream of air (using suction) through a reflux condenser, a sulfuric acid trap, and a Dehydrite drying tube to a combustion furnace where the hydrogen is converted to water by reaction with the CuO filling of the tube. The water is absorbed in a tared absorption tube filled with Drierite, and protected from the air by a guard absorber containing sulfuric acid. When the reaction in the decomposition flask is nearly complete, the solution in the flask is boiled gently until solution is complete, and then for 30 min thereafter. A blank run is made

Metallic Al (oil-, grease-, and water-free basis), per cent

$$\begin{aligned} &= \frac{99.8[(A - B) - 0.00276C]W - 0.01284DW}{W} \\ &= \frac{99.8(A - B)}{W} - 0.275C - 1.282D \end{aligned}$$

where  $A$  = water produced from the sample, in grams,

$B$  = water produced by blank, in grams,

$C$  = percentage of Zn contained in the Al (oil-, grease-, and moisture-free basis, see determination of Zn, p. 1308),

$D$  = percentage of Si contained in the Al (oil-, grease-, and moisture-free basis, see determination of Si, p. 1308), and

$W$  = grams of sample

### ASSAY OF METALLIC ALUMINUM BY EUDIOMETRIC PROCEDURE

**Procedure**—Use a eudiometric assembly such as that shown in Fig. 32.8. Place dilute  $H_2SO_4$  solution (0.2% w/v) in the measuring buret and its leveling bulb and add a few drops of 1% methyl orange solution to improve readability. Saturate the solution with hydrogen and adjust the liquid level so that liquid fills the bore of the three-way stopcock.

Place 100 ml. of 10% w/v NaOH solution in the reaction flask, and saturate it with hydrogen. Weigh a specimen of the aluminum powder that will evolve 470 to 490 cc. of hydrogen at the temperature and pressure (barometric) at which the evolved gas is to be measured. One g. of aluminum generates 1246.6 cc. of hydrogen at 0°C., 760 mm. Hg. Wrap the specimen tightly in filter paper and introduce it into the side neck of the flask, where it is supported by the curved-rod extension of the center neck closure.

Purge the dead space of the assembly for at least 10 min. by introducing a stream of hydrogen at the 2-way stopcock, and allowing it to exit at the 3-way stopcock turned open to the atmosphere. Close the system at atmospheric pressure and then test for leaks by turning the 3-way stopcock to connect the flask and buret and lowering the leveling bulb. When the system has been found to be leak-free, and at least 10 min. have elapsed to allow for saturation of the gas space with water vapor, check the fiducial setting (liquid level in the stopcock). Read the temperature of the assembly and then cause the sample to fall into the alkaline solution by rotating the sample retaining device.

As gas evolution proceeds, lower the leveling bulb to maintain approximate atmospheric pressure.

When the reaction is complete, bring the system to the same temperature as that at the time the reaction began, hold at this temperature for 10 to 15 min., and then read the volume of hydrogen generated. Read the barometric pressure and correct it for temperature of reading.

Metallic aluminum, per cent

$$= \left[ \left( V \times \frac{[P - p]273.2}{760[273.2 + T]} \right) - 3.428AW - 15.976BW \right] \times \frac{0.08022}{W}$$

$$= \frac{0.02884V(P - p)}{W(273.2 + T)} - 0.2750A - 1.282B$$

where  $V$  = hydrogen measured at temperature  $T^{\circ}\text{C}.$ , in cubic centimeters,  
 $P$  = barometric pressure, corrected for temperature, in millimeters of Hg,  
 $p$  = vapor pressure of water, at temperature  $T^{\circ}\text{C}.$  in millimeters of Hg,  
 $T$  = temperature in  $^{\circ}\text{C}.$ ,  
 $W$  = sample in grams,  
 $A$  = percentage of zinc (Zn), and  
 $B$  = percentage of silicon (Si).

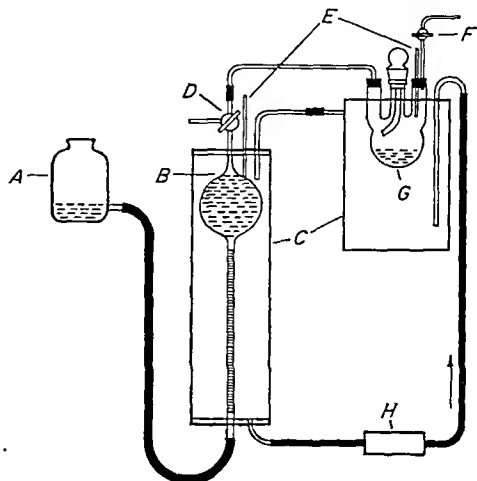


FIG. 32-8. Eudiometer: *A*, Leveling Bottle; *B*, Buret, 500-ml.; *C*, Constant Temperature Baths; *D*, Stopcock, 3-Way; *E*, Thermometers; *F*, Stopcock, 2-Way; *G*, Reaction Flask, 250-ml.; *H*, Circulating Pump.

## VOLATILE AT 105°C

*Procedure*—Determine the per cent of loss in weight of a 2 g sample dried at  $105^{\circ} \pm 3^{\circ}\text{C}$  for 4 hr

## ETHER SOLUBLE MATERIAL

*Procedure*—Extract a 2-g sample with diethyl ether for 4 hr in a Soxhlet apparatus. Evaporate the extract in a tared beaker on a steam bath to constant weight

## SILICON (AS Si)

*Procedure*—Dissolve a 1-g sample in 30 ml of mixed acids (230 ml  $\text{H}_2\text{SO}_4$ , 400 ml  $\text{HCl}$ , 400 ml  $\text{HNO}_3$ , 970 ml  $\text{H}_2\text{O}$ ). Then add 5 ml of concentrated  $\text{H}_2\text{SO}_4$  and 12 ml of concentrated  $\text{HClO}_4$  (70%) and evaporate to copious fumes. Dilute, filter, ignite, weigh, volatilize with  $\text{HF}$  (plus 3 to 4 drops  $\text{H}_2\text{SO}_4$ ), ignite and reweigh. Loss on volatilization  $(\text{SiO}_2) \times 0.4672 = \text{Si}$

## ZINC

*Procedure*—Dissolve a 2 g sample in 20 ml of concentrated  $\text{HCl}$  (Use a larger sample and proportionately more  $\text{HCl}$  if  $\text{Zn}$  content is low). Add 1 ml of concentrated  $\text{HNO}_3$  and boil until all copper is dissolved and brown fumes have been expelled. Dilute to 200 ml, cool to about  $60^{\circ}\text{C}$ , and saturate with  $\text{H}_2\text{S}$ . Filter, wash with dilute (1:99)  $\text{H}_2\text{SO}_4$  saturated with  $\text{H}_2\text{S}$  and discard the precipitate. Boil the filtrate to expel  $\text{H}_2\text{S}$ , cool slightly, add 20 g of tartaric acid, dilute to 300 ml and make neutral with  $\text{NH}_4\text{OH}$  using methyl red as indicator. Add 25 ml of strong formic acid mixture (200 ml  $\text{HCO}_2\text{H}$ , 250 g  $(\text{NH}_4)_2\text{SO}_4$  and 30 ml  $\text{NH}_4\text{OH}$  in water to make 1000 ml), heat nearly to boiling and saturate with a rapid stream of  $\text{H}_2\text{S}$  passed in for 15 min. Allow the precipitate to settle for 2 to 3 hr, filter through a close texture quantitative paper (with added ashless paper pulp) and wash with hot diluted formic acid mixture (strong formic solution specified above diluted 25:1000) saturated with  $\text{H}_2\text{S}$ . Finish the determination gravimetrically or titrimetrically. For the gravimetric method, ignite to  $\text{ZnO}$  in a tared porcelain crucible at  $700^{\circ}\text{C}$ .  $\text{ZnO} \times 0.8034 = \text{Zn}$

For the titrimetric method, dissolve the  $\text{ZnS}$  in hot dilute  $\text{HCl}$  and expel  $\text{H}_2\text{S}$  by boiling. Dilute to 100 ml, neutralize with  $\text{NH}_4\text{OH}$ , add buffer and titrate with standard disodium ethylenediaminetetraacetate solution (EDTA) in the manner described for the assay of  $\text{ZnO}$  p. 1343

$$\text{Zn per cent} = \frac{6.538MV}{W}$$

where  $M$  = molarity of the EDTA solution,

$V$  = volume of EDTA solution used in milliliters, and

$W$  = weight of sample in grams

## IRON

*Procedure*—Transfer to a 600 ml beaker an accurately weighed sample of about 2 g and add 50 ml of concentrated  $\text{HCl}$  a little at a time to control rate of reaction. When vigorous reaction has subsided, add 60 ml of distilled water and boil until reaction is complete.

Add sufficient 5% w/v aqueous solution of  $\text{KMnO}_4$  to ensure oxidation of the iron present (normally a few drops are adequate). Reboil, and then reduce the iron by adding drop-by-drop, a freshly-prepared solution of stannous chloride (15 g. of iron-free  $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$  in 100 ml. of 1:2 HCl) until the yellow color is discharged. Add 1 drop (and no more) of stannous chloride in excess.

Cool the solution in ice water. Then add 10 ml. of a saturated solution of  $\text{HgCl}_2$ , and stir for 1 min. If a fine white precipitate does not form at this stage (or if a dark-colored precipitate forms) the specimen should be discarded and a new determination begun using freshly prepared reagents, and carefully following the specified steps.

Dilute the solution to 300 ml., add 4 ml. of concentrated  $\text{H}_2\text{SO}_4$ , 10 ml. of concentrated  $\text{H}_3\text{PO}_4$ , and 6 to 8 drops of sodium diphenylbenzidine sulfonate indicator solution (0.5% w/v in distilled water). Titrate with 0.02 N  $\text{K}_2\text{Cr}_2\text{O}_7$  solution to a blue or bluish-purple color that persists for at least 60 sec.

Determine a blank on the reagents used.

$$\text{Iron (Fe), per cent} = \frac{5.585N(V - B)}{W} \quad (\text{See Eq. 32-1, p. 1304.})$$

NOTE.—The 0.02 N  $\text{K}_2\text{Cr}_2\text{O}_7$  is a primary standard solution made by dissolving 0.9808 g. of National Bureau of Standards sample No. 136  $\text{K}_2\text{Cr}_2\text{O}_7$  (previously dried at 110°C.) in distilled water to make exactly 1000 ml.

## MAGNESIUM

*Procedure.*—To a 1-g. sample add 70 ml. of hot water, and gradually 20 ml. of 20% NaOH solution. Boil, dilute to 100 ml., filter, and discard the filtrate. Dissolve the residue in 15 ml. of hot 1:1 HCl. Neutralize the excess acid with  $\text{NH}_4\text{OH}$  and continue the conventional gravimetric determination of magnesium by precipitation as phosphate, filtration, ignition, and weighing as  $\text{Mg}_2\text{P}_2\text{O}_7$ .  $\text{Mg}_2\text{P}_2\text{O}_7 \times 0.2185 = \text{Mg}$ .

## COPPER AND LEAD

### ELECTRODEPOSITION METHOD

*Procedure.*—To a 1-g. sample add 75 ml. of water, and then slowly add 25 ml. of 20% NaOH solution. Boil, filter the solution, and wash the residue with hot water. Discard the filtrate. Dissolve the precipitate in 10 ml. of hot 1:1  $\text{HNO}_3$  and dilute to 125 ml. with distilled water. Using tared platinum-gauze electrodes (anode rotating), electrolyze the solution for 20 min. at 2 to 3 amp. Then add 5 ml. of concentrated  $\text{H}_2\text{SO}_4$  and continue electrolysis for 25 min. more. Test for completeness of electrolysis by immersing a small clean cathode area (stem) for several minutes. Remove the electrodes while washing with a gentle stream of distilled water and complete washing by dipping in distilled water and then in ethanol. Dry the cathode at about 70°C. and the anode at about 130°C. Cool and weigh. Retain the solution for nickel determination. Copper is weighed as such; lead as the oxide,  $\text{PbO}_2$ .  $\text{PbO}_2 \times 0.866 = \text{Pb}$ .

### COLORIMETRIC METHOD FOR COPPER

For aluminum samples of low copper content (0.2% Cu or less) the following colorimetric procedure for copper is recommended.

## TIN

*Procedure.*—To a 1-g. sample add 75 ml. of water and then slowly, 25 ml. of 20% NaOH solution. Boil, filter, and wash the residue with hot water. Discard the filtrate. Dissolve most of the precipitate by treating it with boiling-hot 1:1 HCl. Ignite the paper and residue in a porcelain crucible, and add the ash quantitatively to the HCl extract. Add 20 ml. of concentrated  $\text{HNO}_3$  and evaporate nearly to dryness (3 to 5 ml.). Add 10 ml. of  $\text{HNO}_3$  and 50 ml. of hot water, boil, and allow to stand for about 30 min. on a steam bath. Filter through a small quantitative paper. Complete the determination by the  $\text{SnO}_2$ -volatilization procedure described in "Tin Dioxide by Volatilization," p. 1402, under "Propellants."  $\text{SnO}_2 \times 0.7877 = \text{Sn}$ .

## MANGANESE (COLORIMETRIC)

For aluminum samples of low manganese content (0.1% and lower), the colorimetric method, described on p. 1324, for determining manganese in magnesium oxide is recommended. A sample size of about 0.2 g. is appropriate for the 0.1% Mn level. The procedure for aluminum samples is simplified in that these samples do not contain an appreciable amount of chlorides. Hence, chloride removal is not a critical step and the proper (constant) excess of  $\text{AgNO}_3$  solution is achieved merely by adding 5 ml. of the 1% w/v solution.

## AMMONIUM NITRATE

## MOISTURE BY THE KARL FISCHER TITRATION

*Procedure.*—A sample of about 10 g. is weighed accurately by difference from a stoppered vial, and 50 ml. of methanol are used as solvent in the titration cell. The titration may be made directly with the Karl Fischer reagent or by back-titration of an excess of the reagent with standard water-in-methanol solution. For the procedure see "Moisture by Karl Fischer Titration," p. 1290.

## ETHER-SOLUBLE MATERIAL

*Procedure.*—An accurately weighed sample of about 25 g. is extracted with anhydrous diethyl ether for 20 min. in a Soxhlet apparatus using an 80 by 25 mm. paper thimble and a tared receiving flask. The ether is evaporated (hood) by gentle heat (steam bath) and a dry-air jet, and finally the flask is dried to constant weight at 100°C.

## WATER-INSOLUBLE MATERIAL

*Procedure.*—An accurately weighed sample of about 25 g. is transferred to a tared, glass, filtering crucible of fine porosity, 30 by 145 mm., and washed thoroughly with hot distilled water. The residue in the crucible is then washed with cold distilled water, followed by several 15-ml. portions of cold absolute methanol, and finally by four 15-ml. portions of anhydrous diethyl ether. The crucible is dried by suction and then to constant weight at 100°C. Percentage of insoluble material in the sample is calculated from the weight of residue found.

## INSOLUBLE MATERIAL RETAINED ON U S STANDARD

420  $\mu$  (NO. 40) SIEVE

*Procedure.*—An accurately weighed sample of about 100 g is dissolved in hot distilled water in a beaker and the solution is poured through a U S Standard 420  $\mu$  (No. 40) sieve. Insoluble matter is transferred to the sieve by means of a jet of hot distilled water and washed on the sieve with hot water until no more insoluble matter passes through. The sieve and the residue retained on it are dried for 1 hr at 100°C. The residue is transferred to a piece of glazed paper and then to a tared weighing dish. The dish is reweighed and the increase in weight is converted to percentage of insoluble matter in the sample.

## ACIDITY OR ALKALINITY

*Procedure.*—A sample of  $8.0 \pm 0.1$  g is transferred to a 100 ml volumetric flask, and dissolved in recently boiled cold, distilled water. The contents of the flask are made up to the mark and mixed. The pH of the solution is determined at room temperature with a carefully standardized electrometric pH meter.

## NITRITES

*Procedure.*—An accurately weighed sample of 1 g is transferred to a test tube (20 mm diameter) containing 10 ml of distilled water. By means of a buret or pipet with 0.02 ml graduations exactly 0.10 ml of sodium nitrite solution (0.0110 g per liter) is transferred to a similar test tube containing 10 ml of distilled water. To each test tube is added 1 ml of 10% sulfuric acid solution and 1 ml of a freshly prepared colorless 0.5% solution of meta phenylenediamine hydrochloride. (If the meta phenylenediamine solution is colored when prepared, it is decolorized by treatment with animal charcoal.) The solutions in the 2 test tubes are each mixed well, and examined for coloration by looking through the sides of the test tubes against a white background. If the coloration in the sample is not greater than that in the standard tube, the sample contains less than 0.0001% of ammonium nitrite.

## CHLORIDES (VOLHARD PROCEDURE)

*Procedure.*—The appropriate sample size, based on expected ammonium chloride content, is for content below 0.02%, 30 g, for content of 0.02 to 0.20%, 10 g, for content of 0.20 to 0.50%, 5 g. The sample is dissolved in 150 ml of distilled water in a 500 ml Erlenmeyer flask. Eight ml of 1.1  $\text{HNO}_3$  are added and mixed with the solution. A measured excess of at least 5 ml of standard 0.05  $N$  silver nitrate are added from a buret and mixed with the solution by swirling. One ml of nitrobenzene is added, and the flask is vigorously swirled to promote coagulation of the precipitate. After the precipitate has settled, a little more silver nitrate solution is added to the supernatant liquid. If an excess of the standard solution is present, no turbidity will appear. When the supernatant liquid is clear, add 2 to 3 ml of ferric alum indicator and back titrate the excess silver nitrate with 0.05  $N$  potassium thiocyanate to a permanent red brown color. (The indicator is prepared by dissolving 200 g of ferric ammonium sulfate in 300 ml of distilled water, boiling, adding 25 ml  $\text{HNO}_3$  and filtering.)

$$\text{Ammonium chloride (NH}_4\text{Cl), per cent} = \frac{5.35(AN - BN)}{W} \quad (\text{See Eq. 32-4})$$

## SULFATED ASH

**Procedure.**—A 50-ml. porcelain crucible and its cover are ignited for about 30 min. at  $800^{\circ} \pm 25^{\circ}\text{C.}$ , cooled, and reweighed. Three ml. of concentrated  $\text{H}_2\text{SO}_4$  and an accurately weighed sample of about 10 g. are placed in the crucible, the cover is placed upside down on the crucible, and the assembly is heated carefully on a hot plate and asbestos board or sand bath until all the salt has been volatilized (at  $300^{\circ} \pm 25^{\circ}\text{C.}$ ). Then the assembly is placed in a muffle, ignited at  $800^{\circ} \pm 25^{\circ}\text{C.}$  for at least 30 min., cooled, and reweighed. The weight of residue is calculated to percentage of sulfated ash.

## ASSAY BY FORMALDEHYDE METHOD

**Procedure.**—Fifty ml. of 38% reagent formaldehyde and 50 ml. of distilled water are mixed in a 250-ml. Erlenmeyer flask (or beaker). Four drops of 1% phenolphthalein or thymolphthalein indicator solution are added and the solution is neutralized by drop-by-drop addition of carbonate-free 0.2 *N* NaOH solution (pink color, pH = 8.6). An accurately weighed sample of 0.5 to 0.8 g. is dissolved in the neutralized solution, titrated to a pink end point with 0.2 *N* NaOH solution, and an excess of about 2 ml. of the standard alkali is added. The flask is stoppered, permitted to stand for 45 min., and its contents are then back-titrated with 0.05 *N* HCl to a very faint pink end point (pH = 8.0). Alternatively, a pH meter and glass-calomel electrode system may be used, titrating to pH 8.5.

$$\text{Ammonium nitrate (NH}_4\text{NO}_3\text{), per cent} = \frac{8.005(AN - BN')}{W} - 1.496C$$

where *C* = percentage of  $\text{NH}_4\text{Cl}$  in the sample, as determined by the procedure given under "Chlorides (Volhard Procedure)," p. 1312. (See Eq. 32-4.)

## ALTERNATIVE ASSAY BY NITROMETER METHOD

Ammonium nitrate is calculated from the percentage of nitrogen determined by means of a du Pont 5-part nitrometer or equivalent. No corrections for ammonium chloride or ammonium sulfate impurities are necessary. The method is applicable to samples that may contain zinc oxide. An approximately 3-g. sample is crushed so that it will pass completely through a U. S. Standard 149- $\mu$  (No. 100) sieve. Exactly 1 g. of the sieved material is transferred to the cup of the nitrometer. The remainder of the procedure and the standardization of the nitrometer are given under "Nitrogen by Nitrometer Method," Vol. I, p. 755.

## AMMONIUM PERCHLORATE

## MOISTURE BY THE KARL FISCHER TITRATION

**Procedure.**—A sample of about 15 g. is weighed accurately by difference from a stoppered vial, and 100 ml. of dry 1:3 methanol-pyridine mixture are used as solvent in the titration cell. The titration may be made directly with the Karl Fischer reagent or by back-titration of an excess of the reagent with standard water-in-methanol solution. For procedures see "Moisture by Karl Fischer Titration," p. 1290.



## ACIDITY BY pH METER METHOD

*Procedure*—A sample of  $11.8 \pm 0.1$  g is transferred to a 100 ml volumetric flask and dissolved in recently boiled cold distilled water. The contents of the flask are made up to the mark and mixed. The pH of the solution is determined at room temperature with a carefully standardized electrometric pH meter.

## CHLORIDES

*Procedure*—A 20 g sample weighed to the nearest 0.01 g is dissolved in 150 ml of distilled water in a 500 ml Erlenmeyer flask. The Volhard determination of chloride is then completed exactly as described under Chlorides p 1312.

## BROMATES

*Procedure*—Two hundred ml of freshly boiled cold distilled water and 5 ml of concentrated HCl are placed in each of two 500 ml glass stoppered Erlenmeyer flasks. About 0.5 g of sodium bicarbonate is added to each open flask and swirled. Twenty g of sample (weighed to nearest 0.05 g) are added to 1 flask and 5 ml of 0.0200 N potassium iodate solution are pipetted into the other. About 1 g of potassium iodide is added to each flask, the flasks are stoppered and stored in a dark cabinet for 1 hr. The stopper is removed from the flask to which the sample was added, 5 ml of starch indicator are added and the contents are titrated with 0.02 N sodium thiosulfate solution to disappearance of the blue color. The contents of the other flask are titrated in a like manner.

$$\text{Ammonium bromate (NH}_4\text{BrO}_3) \text{ per cent} = \frac{0.243A}{BW}$$

where  $A$  = sodium thiosulfate solution used for the sample in milliliters

$B$  = sodium thiosulfate solution used for titrating 5 ml of 0.0200 N potassium iodate solution in milliliters and

$W$  = weight of sample taken for analysis in grams

## CHLORATES

*Reagents* Ferrous Ammonium Sulfate Solution, Approximately 0.01 N—Add 100 ml of concentrated  $\text{H}_2\text{SO}_4$  to about 500 ml of distilled water, boil the solution and dissolve in it 4.000 g of ferrous ammonium sulfate hexahydrate ( $\text{FeSO}_4 \cdot [\text{NH}_4]_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$ ). Saturate the solution with  $\text{CO}_2$  as it cools to room temperature. When it is cool, make the solution volume to 1000 ml in a volumetric flask using recently boiled and cooled distilled water that has been saturated with  $\text{CO}_2$ . Store the reagent in a dark bottle and prepare fresh if the available solution is more than 1 week old or if it shows visible evidence of oxidation.

Potassium Permanganate Standard 0.01 N Solution—Dilute 100 ml of a stock 0.1 N  $\text{KMnO}_4$  solution with freshly boiled and cooled distilled water to make 1000 ml and store the solution in a dark bottle. Standardize in the conventional manner against a 0.01 N sodium oxalate solution prepared by dissolving 0.6700 g of dry reagent (National Bureau of Standards No. 40e) in 1000 ml of distilled water.

*Procedure*—Place 30 ml of distilled water in a 300 ml iodine flask having a standard taper neck. Boil the water for a few seconds and add 20 to 40 ml of 0.01 N ferrous ammonium sulfate solution. The amount of ferrous solution added should be in substantial excess of the amount required for reaction with the

chlorates of the sample. Bring the solution to boiling again and add 2.00 g. of sample through a dry powder funnel. Attach the flask to a reflux condenser and reflux the sample solution for 10 to 12 min. Disconnect the flask from the condenser and back-titrate the excess ferrous ammonium sulfate with standard 0.01  $N$   $KMnO_4$  solution. Make a blank determination on the same amounts of reagents as those used for the analysis of the sample.

$$\text{Ammonium chlorate (NH}_4\text{ClO}_3\text{), per cent} = \frac{1.69N(A - V)}{W} - 0.70B$$

where  $N$  = normality of the standard 0.01  $N$   $KMnO_4$  solution,

$A$  = volume of standard  $KMnO_4$  solution required by the blank in milliliters,

$V$  = volume of standard  $KMnO_4$  solution required by the sample in milliliters,

$W$  = weight of sample in grams, and

$B$  = percentage of ammonium bromate in the sample, as determined by the procedure described in the preceding section.

### ETHER-SOLUBLE MATERIAL

The determination of material soluble in diethyl ether is performed exactly as described under "Ammonium Nitrate," "Ether Soluble Material," p. 1311.

### WATER-INSOLUBLE MATERIAL

The determination of insoluble material is performed exactly as for "Ammonium Nitrate," "Water-Insoluble Material," p. 1311.

### SULFATED ASH

The determination of sulfated ash is performed exactly as for "Ammonium Nitrate," "Sulfated Ash," p. 1313.

### ASSAY BY SODIUM CARBONATE FUSION (VOLHARD TITRATION METHOD)

*Procedure.*—An accurately weighed sample of about 0.5 g. is added to a 40-ml. platinum crucible containing approximately 5 g. of sodium carbonate, and mixed carefully to avoid mechanical loss of sample. The crucible is nearly filled with sodium carbonate using a known weight so that a correction can be made for the chlorine impurity of the carbonate. The sodium carbonate is gradually fused over a low flame for about 30 min. and then heat is slowly increased until the full flame of a Meker burner is in use. When fusion is complete, the melt is cooled and dissolved in a covered beaker containing distilled water and an excess (usually about 35 ml.) of 1:1  $HNO_3$ . The solution is quantitatively transferred to a 500-ml. Erlenmeyer flask and diluted with water to about 150 ml. Exactly 50 ml. of 0.1000  $N$   $AgNO_3$  (primary standard solution) are measured into the solution by pipet or buret while the solution is agitated by swirling. The Volhard determination of chlorides is then completed as described above, p. 1312.

Alternatively, the titration may be made potentiometrically using a silver indicator electrode system, and obtaining the end point directly with silver nitrate as titrant.

$$\text{Ammonium perchlorate (NH}_4\text{ClO}_4\text{), per cent} = \frac{11.75(AN - BN')}{W} - 2.20C - 1.16D$$

where  $C$  = percentage of ammonium chloride found by procedure given for "Chlorides,"  
 p 1314, and  
 $D$  = percentage of ammonium chlorate found by procedure given for "Chlorates,"  
 p 1314 (See Eq 32-4)

### 1,1-DIMETHYLHYDRAZINE (UDMH, UNSYMMETRICAL DIMETHYLHYDRAZINE)

#### ASSAY

*Procedure*—Using a sample of 0.50 to 0.60 g in a sealed glass ampoule, determine the content of unsymmetrical dimethylhydrazine (UDMH) by titration with standard 0.1  $M$  potassium iodate solution following the potentiometric procedure described under the assay method for hydrazine p 1317. In the case of the 1,1 dimethylhydrazine the temperature throughout the titration should be maintained in the range  $-5^{\circ}$  to  $+10^{\circ}\text{C}$  and the titration should be completed within a total time of 5 min. At the end point the solution will be light yellow and the steep potential increase will be in the range 0.67 to 0.70 volts

$$\text{UDMH per cent} = \frac{12.02AM}{W}$$

where  $A$  = standard 0.1  $M$  iodate solution used in milliliters,  
 $M$  = molarity of the iodate solution, and  
 $W$  = weight of sample taken for analysis in grams

#### MELTING POINT

*Procedure*—Use a capillary melting point tube (1.5 to 2.0 mm by 90 mm) filled by means of a small tuberculin hypodermic syringe and a stainless steel spinal needle (20 gauge  $3\frac{1}{2}$  in long) and avoid getting any sample on the upper part of the capillary. Seal off the tube about 1 cm from the open end using a very small hot flame and avoiding contamination of the tube contents with combustion gases. Place acetone in an unsilvered Dewar flask to a depth of about 100 mm and add bits of dry ice until the temperature is in the range  $-62^{\circ}$  to  $-64^{\circ}\text{C}$ . Freeze the sample attached to a low temperature ASTM No. 6C thermometer ( $-80^{\circ}$  to  $+20^{\circ}\text{C}$  in  $1^{\circ}\text{C}$  divisions 76 mm immersion) in an acetone dry ice mixture and immerse it in the liquid in the Dewar flask to the 76-mm immersion mark. Allow the temperature in the Dewar flask to rise at a rate not greater than  $1.0^{\circ}\text{C}$  per min (preferably  $0.5^{\circ}$  to  $0.8^{\circ}\text{C}$  per min) and record the temperature at which the sample becomes completely liquid. Calibrate the thermometer by taking the melting point of pure chloroform ( $-63.5^{\circ}\text{C}$ ) in a capillary and apply a suitable correction for any difference found to the melting point of the dimethylhydrazine.

#### DISTILLATION RANGE

The vapor temperatures are recorded when 10 ml and 90 ml have been collected in the receiving graduate on distilling a 100 ml sample in a special distillation assembly described in military specification M1D 2560-1B. Details of the equipment and procedure are given in the cited specification but, for reasons of space, are not reproduced here.

## WATER

Maximum water content may be calculated from the 90-ml. distillation temperature as follows:

Weight per cent water

$$= 0.14 [(\text{corrected 90-ml. distillation temperature in } ^\circ\text{F.}) - (146^\circ\text{F.})]$$

Since the maximum water content usually allowed is 0.3%, it can be calculated that the temperature at the 90-ml. recovery point cannot exceed 148.1°F. if the water-content limitation is met.

Alternatively, water may be determined spectrophotometrically by the method described for the alternative procedure for water below, p. 1318, using the peak for water in the near infrared at 1.9  $\mu$  and with a pure water-free sample of 1,1-dimethylhydrazine in the reference cell.

## HYDRAZINE

## HYDRAZINE CONTENT (ASSAY)

**Reagent. Standard Potassium Iodate Solution.**—Dissolve 21.402 g. of potassium iodate (dried at 180°C.) in distilled water and dilute to 1000 ml. in a volumetric flask. Dissolve exactly 0.5000 g. of pure dry hydrazine sulfate in a cooled solution of 85 ml. of concentrated hydrochloric acid and 50 ml. of water in a 500-ml. iodine flask. Titrate with iodate solution in the manner described for assay of hydrazine content of a sample. The 0.5000 g. sample of pure hydrazine sulfate is equivalent to 0.1232 g. hydrazine.  $F = 0.1232$  per milliliter of potassium iodate solution = grams of hydrazine equivalent per milliliter of iodate solution.

$$(1 \text{ ml. of } 0.1 \text{ } M \text{ KIO}_3 \text{ solution} = 0.01301 \text{ g. N}_2\text{H}_4\text{H}_2\text{SO}_4 = 0.003205 \text{ g. N}_2\text{H}_4)$$

**Procedure.**—Fill a tared glass ampoule with chilled sample and seal the tip of the capillary in a small flame. Weigh the filled ampoule containing 0.10 to 0.15 g. of sample, and place it in a heavy-walled glass-stoppered flask (or bottle) containing a cooled solution of 85 ml. of concentrated HCl and 50 ml. of distilled water. Pulverize the ampoule and titrate the solution with standard 0.1  $M$   $\text{KIO}_3$  solution with frequent shaking until the iodine color just begins to fade. Add 10 ml. of chloroform and shake the stoppered flask vigorously. Titrate slowly, drop by drop near the end point, and with thorough shaking between additions of reagents. Finish the titration to complete discharge of the purple color in the chloroform layer. Alternatively (and preferably), the titration may be performed potentiometrically (omitting addition of chloroform in this case), using a calomel-platinum electrode system and plotting milliliters vs. e.m.f. to locate the point of greatest inflection.

$$\text{Hydrazine, per cent} = \frac{100AF}{W}$$

where  $A$  = standard 0.1  $M$  potassium iodate solution in milliliters,

$F$  = hydrazine equivalent per milliliter of potassium iodate solution in grams, and

$W$  = weight of sample taken for analysis in grams.

than 50-ml. increments. Allow the major portion of each increment to decompose before adding any more. If the solution is maintained at its boiling point, the decomposition operation requires 2 to 4 hr. When the peroxide is almost decomposed, transfer the solution to a clean 1000-ml. Pyrex boiling flask, covered with a clean ribbed watch glass. Place a small piece of clean platinum in the boiling flask to prevent concentrating the undecomposed peroxide, and boil the solution until it is condensed to a 25- to 50-ml. volume. Transfer the remaining solution to a 100-ml. platinum evaporating dish in an oven at 105° to 110°C. for a minimum of 1 hr. after all the solution is evaporated.

Determine a blank on 500 ml. of distilled water following all the steps of the above described procedure, except for addition of the peroxide.

$$\text{Evaporation residue, milligrams per liter} = \frac{A - B}{0.3}$$

where  $A$  = residue from the 300 ml. of peroxide and 500 ml. of distilled water, in milligrams, and

$B$  = residue of blank on 500 ml. of distilled water, in milligrams.

### STABILITY

**Procedure.**—Prepare test flasks as follows: dry new 100-ml. Pyrex volumetric flasks and obtain tare weights (to 0.01 g.) with the tops covered by small clean pieces of aluminum foil. Set aside the aluminum covers (in a manner so that each is identified for replacing on the flask to which it belongs), fill the flasks with concentrated high-purity  $\text{HNO}_3$ , cover the tops of the flasks with small beakers, and maintain at 100°C. for 24 hr. Rinse the flasks with distilled water and then immediately with hydrogen peroxide. Screen the flasks by performing the stability test described below, using peroxide from the same container in each flask, and rejecting those flasks which give inconsistent results. (Do not rinse with distilled water after this test; use the flasks for peroxide only.)

Place approximately 80 ml. of peroxide sample to be tested in each of at least 3 tared, specially-prepared, 100-ml. Pyrex volumetric flasks, and immediately cover the tops with the matching pieces of aluminum foil, making the foil concave across the opening so that condensed droplets are prevented from escaping. Reweigh the flasks to 0.01 g. Place the flasks in a boiling-water or steam bath so that the contents are maintained at  $100^\circ \pm 1^\circ\text{C}$ . The upper portion of the necks of each flask must project above the top of the steam bath and be sealed against steam so that steam cannot enter the top of the flask. These steps may be accomplished by using a bath with circular openings equipped with sets of concentric rings (discs) and using a split rubber stopper to fit around the neck of the flask and into the opening of a ring (disc) of appropriate size. At least  $2\frac{1}{2}$  in. of the necks of the flasks should extend above the steam seal to provide adequate condensing surface for the peroxide. After 24 hr. at 100°C., cool, and reweigh the flasks.

$$\text{Active oxygen loss, per cent} = \frac{100(W_1 - W_2)}{0.470CW_3}$$

where  $W_1$  = initial weight of flask, sample, and cover in grams,

$W_2$  = final weight of flask, contents, and cover in grams,

$W_3$  = initial net weight of  $\text{H}_2\text{O}_2$  sample in grams, and

$C$  = weight fraction  $\text{H}_2\text{O}_2$  (concentration, percentage of  $\text{H}_2\text{O}_2$  by weight divided by 100).

from the peroxide sample into the HCl in the 50-ml. volumetric flask, and rinse the beaker with the ammonium chloride-gelatin solution, adding the rinsings to the volumetric flask. Make up to the 50-ml. mark with distilled water. Place a portion of the solution in a polarographic cell, purge with nitrogen for 5 min. and polarograph from  $-0.3$  to  $-0.9$  volts versus a saturated calomel electrode. Calculate the tin content of the sample by reference to a standard curve prepared by treating 0-, 3-, 5- and 8-ml. portions of the standard tin solution exactly as the sample, and then polarographing.

### MAGNESIUM, POWDERED

#### VOLATILE AT $105^{\circ}\text{C}$ .

*Procedure.*—Heat a 5.000-g. sample at  $105^{\circ}\text{C}$ . for 3 hr., cool, and reweigh.

#### OIL AND GREASE

*Procedure.*—Extract a 50.00-g. sample with diethyl ether for 1 hr. in a Soxhlet apparatus. Filter the solution, evaporate on a steam bath, and weigh the residue. Make a blank determination on the ether.

#### CARBIDES

*Apparatus.*—The apparatus consists of a Pyrex reaction flask, suction filtration type, with the side arm connected to a delivery tube leading through a 2-hole stopper to the bottom of a large test tube. The top of the flask carries a 2-hole rubber stopper, through which is inserted a nitrogen-delivery tube (extending to near the bottom of the flask) and a short-stem dropping funnel.

*Procedure.*—Transfer a 50-g. sample to the generating flask and place 50 g. of cuprous chloride in the receiving test tube. Pass nitrogen through the apparatus to remove the air, and continue the nitrogen flow throughout the determination. Lower the test tube and add 15 ml. of concentrated  $\text{NH}_4\text{OH}$  and 30 ml. of hydroxylamine hydrochloride reagent (0.25 g. of gelatin in hot water diluted to 500 ml., plus 500 ml. of 95% ethanol and 1.25 g. of hydroxylamine hydrochloride). Raise the test tube, insert its stopper, and add 100 ml. of distilled water to the flask by means of the dropping funnel. Using a small electric hot plate, heat the mixture in the reaction flask just to boiling.

A red or pink coloration of the solution in the test tube is interpreted as evidence that the magnesium contains more than 0.004% carbides. If the solution in the test tube becomes blue (because of entry of some air), it must be treated with small increments of hydroxylamine hydrochloride reagent until the blue color is discharged.

#### MATERIAL INSOLUBLE IN SULFURIC ACID

*Procedure.*—Treat a 5.000-g. sample with 150 ml. of dilute (1:5)  $\text{H}_2\text{SO}_4$ . Filter the solution through a tared filtering crucible and wash with hot water. Dry and reweigh the crucible and residue. Retain the filtrate for determination of total iron.

#### METALLIC IRON

*Procedure.*—Extract the metallic iron from a 100-g. sample by means of a magnet. Brush the magnetic particles onto glazed paper, and separate the adhering mag-

nesium as much as possible by manipulating the magnet under the paper. Weigh the magnetic material. If the weight exceeds that allowed by the specification determine the iron content by dissolving the iron in  $\text{H}_2\text{SO}_4$ , passing the solution through a Jones reductor (activated zinc amalgam) and titrating with 0.02  $\text{N}$   $\text{KMnO}_4$  solution

$$\text{Metallic iron, per cent} = \frac{5.585 V}{W} \quad (\text{See Eq. 32.2})$$

### TOTAL IRON

**Procedure**—Transfer the filtrate from the determination of insoluble matter to a 300 ml Erlenmeyer flask, add a spiral of aluminum wire, cover with a small watch glass and boil for about 10 min. Cool the flask under a faucet, remove the aluminum spiral and titrate immediately with 0.05  $\text{N}$   $\text{KMnO}_4$  solution. Make a blank determination on the aluminum using 200 ml of 1.5  $\text{H}_2\text{SO}_4$ .

$$\text{Total iron as Fe}_2\text{O}_3 \text{ per cent} = \frac{7.98 A(V - B)}{W} \quad (\text{See Eq. 32.1})$$

### ALUMINUM

**Procedure**—(For about 10% aluminum content) Dissolve a 0.4 g sample by adding 10 ml of concentrated  $\text{H}_2\text{SO}_4$ , followed by small increments of water and adding a little  $\text{HNO}_3$  if necessary to clear. Filter if necessary and add 25 ml of saturated  $\text{NH}_4\text{Cl}$  solution. Heat to boiling and add 1.4  $\text{NH}_4\text{OH}$  until just neutral to methyl red. Filter, redissolve the precipitate in 1.4  $\text{HCl}$ , heat to boiling, and reprecipitate. Filter and wash on quantitative paper. Ignite gently and then at not less than  $1000^\circ\text{C}$  for 1 hr. Cool and reweigh rapidly as  $\text{Al}_2\text{O}_3$ .  $\text{Al}_2\text{O}_3 \times 0.5291 = \text{Al}$

### FREE METALLIC MAGNESIUM, BY WATER CONVERSION

**Procedure**—A 1.000 g sample is treated in a generating flask with 30%  $\text{H}_2\text{SO}_4$ . The generated hydrogen is swept through a drying train (by air suction) into a tube furnace where the hydrogen is converted to water by reaction with a  $\text{CuO}$  filling in the tube and the water is absorbed in a tared absorption tube containing Dehydrite (or equivalent). When the reaction is nearly complete the solution in the generating flask is gently boiled for 30 min and then air is drawn through for an additional 30 min to complete purging of the hydrogen.

$$\text{Metallic Mg, per cent} = \frac{135.0(A - B)}{W}$$

where  $A$  = gain in weight of water absorption tube in grams,  
 $B$  = gain in weight of blank in grams, and  
 $W$  = sample in grams

Details of the procedure are given in military specification JAN M 382 A

### FREE METALLIC MAGNESIUM BY EUDIOMETRIC PROCEDURE

Alternatively magnesium may be determined by measuring the volume of hydrogen evolved by acid treatment. Use an eudiometric assembly such as that shown in Fig. 32.8 and in general the procedure given above for determination

of metallic aluminum by the eudiometric procedure (p. 1306), with the following exceptions. Use 100 ml. of 3% v/v  $\text{H}_2\text{SO}_4$  as the reacting solvent. One g. of magnesium will generate 921.66 cc. of hydrogen at standard conditions,  $0^\circ\text{C}.$ , and 760 mm. Hg pressure.

$$\text{Free metallic Mg (uncorrected for other metals), per cent} = \frac{0.03900V(P-p)}{W(273.2 + T)}$$

where  $V$  = reading of gas buret, hydrogen at  $T^\circ\text{C}.$  in cubic centimeters,  
 $P$  = barometric pressure, corrected for temperature in millimeters of Hg,  
 $p$  = vapor pressure of water, at temperature  $T^\circ\text{C}.$  in millimeters of Hg,  
 $T$  = temperature,  $^\circ\text{C}.$ , and  
 $W$  = sample, in grams.

## MAGNESIUM OXIDE

### ASSAY

*Procedure.*—An 0.18-g. sample is dissolved in acetic, nitric, and sulfuric acids and taken to fumes of  $\text{SO}_3$  by heating. Magnesium is precipitated as the hydroxide with 6% w/v NaOH, filtered out, and redissolved in 1:1 HCl. The solution is neutralized with  $\text{NH}_4\text{OH}$  and 15 ml. of pH 10 buffer added ( $\text{NH}_4\text{Cl}$ , 54 g.;  $\text{NH}_4\text{OH}$ , 350 ml.; and distilled water to make 1000 ml.). It is then titrated with 0.1  $M$  disodium ethylenediaminetetraacetate (EDTA) solution with Eriochrome Black T as indicator.

$$\text{Magnesium oxide (MgO), per cent} = \frac{4.320MV}{W} - 0.719 A$$

where  $M$  = molarity of the EDTA solution,  
 $V$  = volume of the EDTA solution in milliliters,  
 $W$  = weight of sample in grams, and  
 $A$  = percentage of CaO found in an independent determination.

The molarity of the EDTA is determined by titration against a sample of reagent grade zinc as described under "Zinc Oxide," p. 1343.

## CARBONATES AS $\text{CO}_2$

*Procedure.*—A 10- to 12-g. sample is placed in a wide mouth rubber-extraction flask and moistened with  $\text{CO}_2$ -free distilled water. The flask is closed by a 3-hole rubber stopper providing; (1) an inlet for a measured flow (flowmeter) of  $\text{CO}_2$ -free inert gas (e.g., helium or nitrogen); (2) an inlet (separatory funnel) for introduction of acid; and (3) an outlet for escape of gas through a vertical condenser. From the condenser the gas flow passes through a train having in sequence: a gas-washing bottle (bubbler) containing concentrated  $\text{H}_2\text{SO}_4$ ; a U-tube containing dehydrated cupric sulfate on pumice, for removal of  $\text{H}_2\text{S}$  and HCl; a U-tube filled with  $\text{Mg}(\text{ClO}_4)_2$  for removal of last traces of  $\text{H}_2\text{O}$ ; and a tared U-tube filled partly with Ascarite and partly with  $\text{Mg}(\text{ClO}_4)_2$ , the latter on the exit side. After the assembly has been flushed for a suitable period, the tared U-tube is attached and the sample is decomposed by addition of 50 ml. of concentrated HCl through a separatory funnel. The sample solution is boiled for a few minutes, then allowed to cool for 20 min. with the inert gas flowing at 50 to 70 ml. per min. throughout



the determination. The gain in weight of the tared U tube is due to  $\text{CO}_2$  absorption and is used, after correction for a reagent blank, for calculation of the percentage of  $\text{CO}_2$  in the sample.

### CALCIUM OXIDE ( $\text{CaO}$ )

$\text{CaO}$  is determined by the EDTA method or the flame photometer procedures as described in Vol I, pp 600-605

### SILICA ( $\text{SiO}_2$ ), CHLORIDES ( $\text{Cl}^-$ ), SULFATES ( $\text{SO}_4^{2-}$ ), ACID INSOLUBLES, IGNITION LOSS AT $800^\circ\text{C}$ , AND MOISTURE (LOSS AT $200^\circ\text{C}$ .)

All are determined by conventional gravimetric or titrimetric procedures

### IRON OXIDE ( $\text{Fe}_2\text{O}_3$ )

Iron oxide is determined by titration with standard 0.02 N  $\text{K}_2\text{Cr}_2\text{O}_7$  solution using sodium diphenylbenzidinesulfonate as indicator

### MANGANESE (Mn) (COLORIMETRIC)

**Reagents** Mixed Acid Solution—Add 100 ml of concentrated  $\text{H}_3\text{PO}_4$  to 200 ml of concentrated  $\text{H}_2\text{SO}_4$ . Cool and add slowly 50 ml of concentrated  $\text{HNO}_3$ .

**Dilute Standard  $\text{KMnO}_4$  Solution**—Using standardized  $\text{KMnO}_4$  solution prepare a dilute standard solution to contain 0.0100 g Mn per liter (1 liter of 0.1 N  $\text{KMnO}_4$  contains 3.161 g  $\text{KMnO}_4$  equivalent to 1.099 g Mn)

**Preparation of Standard Curve**—Measure from a buret a series of portions of the standard dilute  $\text{KMnO}_4$  (eg 0.5, 1.0, 1.5, 2.0 and 3.0 ml covering the range 0.0 to 0.00030 g of Mn) placing each portion in a separate 400 ml beaker. To each beaker add 5.0 ml of the mixed acid solution and sufficient distilled water to bring the total volume to about 60 ml. Heat to boiling and develop the pink color as for analysis of a sample using 5.0 ml of  $\text{AgNO}_3$  solution and 1.5 to 2 g of the ammonium persulfate. Cool the solutions, make to 100 ml, take transmittance readings at 505  $\text{m}\mu$  and plot transmittance values versus Mn content in grams.

**Procedure**—To a 5.00 g sample in a 400 ml beaker add 25 ml of distilled water. Add 8 to 10 ml of mixed acid solution to 25 ml of distilled water and then gradually add the diluted acid to the sample slurry. Boil the solution for 10 to 15 min. From the value obtained from a chloride determination, calculate the amount of 1% w/v  $\text{AgNO}_3$  solution required to precipitate the chlorides present in the portion of sample taken for analysis. To the boiling solution of sample add gradually (from a small buret or Mohr pipet) the calculated amount of  $\text{AgNO}_3$  solution plus a slight excess (0.5 to 1 ml excess only). Continue boiling several minutes and then let the beaker stand on a steam bath for 20 to 30 min.

Filter the solution through a fine textured paper and test the filtrate for chlorides by adding a few drops of  $\text{AgNO}_3$  solution. If chloride precipitation is found to be incomplete, add 0.5 to 1 ml more of the  $\text{AgNO}_3$  solution and repeat the settling and filtration steps. After chlorides have been completely removed, add  $\text{AgNO}_3$  solution in the amount that will provide a total excess of  $\text{AgNO}_3$  solution within the range of 4 to 5 ml. The filtrate at this stage must be perfectly clear, and must contain not less than 4 ml nor more than 5 ml of  $\text{AgNO}_3$  reagent in

excess of that required for chloride removal. Wash the beaker and filter paper with 3 or 4 small portions (5 to 10 ml. each) of distilled water, avoiding the use of an amount of wash water that would cause the final volume of solution to exceed 100 ml.

Bring the filtered solution to incipient boiling and add (in several small portions) 1.5 to 2 g. of solid ammonium persulfate,  $(\text{NH}_4)_2\text{S}_2\text{O}_8$ . Boil for 60 to 90 sec., cool to 25°C., and make the volume of solution to 100 ml. with distilled water.

Determine the transmittance of the pink solution at a wavelength of 505  $\text{m}\mu$  using a suitable spectrophotometer or a colorimeter provided with a 505  $\text{m}\mu$  interference filter. By reference to the standard curve, read off the weight of Mn corresponding to the observed transmittance value of the sample, and calculate to percentage of Mn.

## NITRIC ACID, FUMING (WHITE OR RED)

### SAMPLING PROCEDURES

**Glass Oleum Bulb.**—Drill a  $\frac{1}{8}$ -in. hole in the center of the bowl of a metal tablespoon. With the spoon held horizontally, with its concave surface upward, insert the capillary of a tared glass oleum bulb downward through the hole. Warm the bulb slightly by passing a small sootless flame near it a few times and insert the capillary tip in the chilled acid sample. Pile powdered dry ice around the bulb in the spoon. When a sufficient sample has been drawn into the bulb, withdraw the capillary tip from the acid and invert the spoon so that the bulb and dry ice are held by a thick cloth in the palm of one hand. The bulb will continue to cool and suck the capillary free of acid. (Otherwise, difficulties are encountered in trying to seal the capillary.) Seal the tip of the capillary in a small hot flame, holding the bulb in the dry ice until the capillary has cooled thoroughly. Allow the bulb to return to room temperature and to dryness in a desiccator, and reweigh.

**Teflon Cell.**—By means of simple shop equipment (drill press and small lathe), construct from Teflon rod stock the cell assembly (consisting of cylindrical cup, "capillary" plug, and cap) shown in Fig. 32-9(a). Weigh the dry Teflon cell assembly at room temperature. By means of a Teflon syringe, transfer a suitable amount of the chilled acid sample to the cup, insert the capillary plug, and close with the cap. Reweigh rapidly, and immediately chill the cell and contents by packing powdered dry ice around it nearly to the top of the cup. Hold the sample in the dry ice bath for 10 to 15 min. before using it for the determination of total acidity.

If a Teflon syringe is not readily available, one may be constructed in the shop from rod stock or, as a temporary expedient, one may be fashioned from tubing and rod stock as illustrated in Fig. 32-9(b). **Caution.**—Because nitric acid and acetone can react with explosive violence if they come together, the dry ice is used alone in all chilling operations; *no acetone* is added to the chilling baths.

### TOTAL ACIDITY

For white or red fuming nitric acid containing no HF, either glass ampoules or Teflon cells may be used in the determination of total acidity. For white or red

fuming nitric acid containing HF, Pyrex glass ampoules may be used where the highest possible accuracy is not required, but otherwise, the Teflon syringe and Teflon cell for weighing samples are considered necessary

**Procedure**—Use a sample size that will consume not less than 40 ml of standard alkali. The standard (carbonate free) NaOH solution may be 0.5 *N* to 1.5 *N*

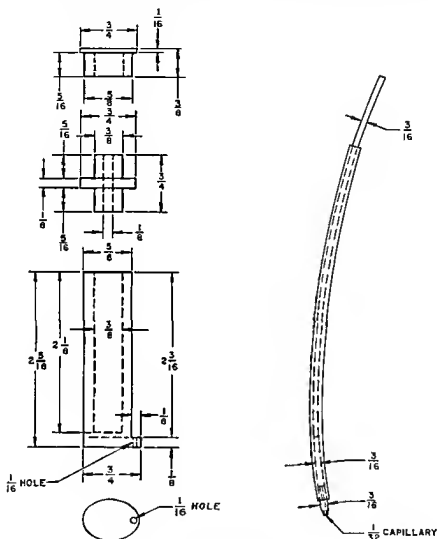


FIG. 32.9 At Left, 3 Part Teflon Cell. At Right, Teflon Syringe Made from Laboratory Stock Items (All Dimensions in Inches)

For 0.5 *N* alkali, the sample size should be about 1.3 g and for 1.5 *N* it should be about 3.9 g. Place a measured amount (in small excess calculated on the sample weight and nominal content or based on a preliminary determination) of standard alkali solution in a heavy walled, glass stoppered, 500 ml iodine flask (e.g. Corning Glass Works, item No. 92930 custom made), bring the total volume of liquid to 150 to 200 ml by adding distilled water, and cool the solution until ice begins to form in it.

If a glass ampoule or oleum bulb is used for the sample, drop it into the cold alkali solution, add a few glass marbles or stoppers, close the flask, and break the bulb by shaking the flask. Allow the flask to stand 5 to 10 min. with occasional shaking. Add a few milliliters of water to the gallery around the stopper, loosen the stopper, and rinse it with distilled water. Pulverize the ampoule capillary thoroughly with a heavy glass rod. Remove and rinse the rod. Back-titrate the excess alkali with standard 0.1  $N$   $H_2SO_4$  to a colorless (or very pale pink) end point using phenolphthalein as indicator. After completion of the titration, make the solution slightly alkaline by adding about 1 ml. of the standard alkali solution, and retain the sample solution for the determination of  $NO_2$ .

If the Teflon cell is used, remove the cap from the chilled cell containing the sample, drop the cap into the chilled standard alkali solution, and slide the cell into the flask held at about a  $45^\circ$  angle, with the capillary of the cell entering the flask first. Stopper the flask, allow diffusion to take place through the capillary with occasional shaking as necessary, and allow the flask to stand 5 or 10 min. after diffusion appears complete, as judged by the color observed by looking through the flask into the capillary. Place a little distilled water in the gallery of the flask, loosen the stopper, rinse it with water, and remove it. Pour most of the solution into a casserole or large beaker. Fish out the cell by means of a coarse platinum-wire hook inserted in the hole in the base of the cell (or in a platinum wire loop attached to the base), rinsing the cell with a jet of distilled water as it is withdrawn. Rinse the contents of the cell into the casserole (or beaker), removing and rinsing the capillary plug to recover any traces of acid or alkali held in the interstices. Transfer the alkaline solution and washings back to the flask quantitatively and back-titrate with standard 0.1  $N$  acid as described above.

$$\text{Total acidity as } HNO_3, \text{ per cent} = \frac{6.302(AN - BN')}{W} \quad (\text{See Eq. 32-4.})$$

### NITROGEN DIOXIDE, $NO_2$

#### ROUTINE PROCEDURE (CERIC AMMONIUM SULFATE-FERROUS AMMONIUM SULFATE TITRATION)

*Procedure.*—Chill the solution from the determination of total acidity by immersing it for several minutes in the dry ice bath and add without agitation an excess of standard 0.1  $N$  ceric ammonium sulfate solution dispensed from a buret with an extended tip immersed in the sample solution to a depth of about  $\frac{1}{4}$  in. from the bottom of the flask. The amount required to give an excess may be determined by a pilot titration. Raise the tip of the buret above the surface of the liquid in the flask and rinse it with distilled water. Stopper the flask, place it in the dry ice bath for several minutes, remove the flask from the dry ice bath, and shake the flask vigorously. Loosen the stopper and rinse it with distilled water. Add 2 drops of ferroin indicator and back-titrate the excess ceric reagent with standard 0.05  $N$  ferrous ammonium sulfate solution (in 0.5  $M$   $H_2SO_4$ ) to an orange-red end point.

$$\text{Nitrogen dioxide, } NO_2, \text{ per cent} = \frac{4.601(AN - BN')}{W} \quad (\text{See Eq. 32-4.})$$

The procedure described above is rapid and convenient, but is subject to several kinds of error, particularly if the solution is not kept sufficiently cold, or if other

tion containing 50  $\mu\text{g}$ . of fluoride ion per milliliter with some water, add 5 ml. of the diluted zirconium-alizarin reagent, and bring to the mark with water.

In still another 50-ml. volumetric flask, place 5 ml. of the diluted zirconium-alizarin reagent and bring to the mark with water. Allow the solutions in the three 50-ml. volumetric flasks to stand for 90 to 100 min.

Set the spectrophotometer or colorimeter at 525  $m\mu$ . Using 1-cm. cells, set the instrument to read 100% transmission with the solution made by mixing 5 ml. of the stock sodium fluoride with zirconium-alizarin reagent. Determine the transmittance of the remaining 2 solutions in the 50-ml. volumetric flasks. Calculate the percentage of HF in the fuming  $\text{HNO}_3$  by means of these results and a calibration curve.

Prepare the calibration curve using the color development and measuring procedures described above, and synthetic mixtures of appropriate known amounts of standard sodium fluoride solution with white or red (as appropriate) fuming  $\text{HNO}_3$  (HF-free). Use the decolorized solution containing 50  $\mu\text{g}$ . of fluoride ion as before in making the 100% transmission setting. Plot the differences in transmittance between sample solutions and the unbleached solution against fluoride concentration.

### TOTAL SOLIDS

*Procedure.*—Using a pipet with a tip sufficiently coarse to pass all suspended matter, transfer a 10-ml. portion of the thoroughly agitated  $\text{HNO}_3$  sample to a tared platinum dish which has been heated to 1200°C. and cooled in a desiccator. Evaporate the acid in a hood on a steam bath or hot plate. Ignite the dish over a low flame to expel the last traces of acid and oxides of nitrogen, and then over a Meker burner or in a muffle furnace at 1200°C. Cool and reweigh.

Total solids equivalents are calculated as follows:

As percentage of  $\text{HNO}_3$  = 3.71  $R$  (for samples from aluminum containers)

= 2.37  $R$  (for samples from stainless steel containers);

As percentage of metal nitrates = 4.18  $R$  (for samples from aluminum containers)

= 3.03  $R$  (for samples from stainless steel containers);

where  $R$  = percentage of solids on ignition

$$= \frac{\text{grams solids} \times 100}{\text{milliliters of sample} \times \text{specific gravity of sample}}$$

Alternatively, determine the content of suspected metallic compounds such as those of iron, aluminum, chromium, and nickel by well known gravimetric or colorimetric procedures, and calculate their nitric acid equivalents.

### FREE NITRIC ACID, $\text{HNO}_3$

Free nitric acid,  $\text{HNO}_3$ , per cent = [percentage of total acidity as  $\text{HNO}_3$ ]

— [1.3697(percentage of  $\text{NO}_2$ )]

— [3.1494(percentage of HF)]

— [ $\text{HNO}_3$  equivalent of metals]

H<sub>2</sub>SO<sub>4</sub>. The sample must be dissolved in the acid, either in the weighing bottle or in the cup of the generator, before it is drawn into the generating bulb, and both the weighing bottle and the cup of the generator must be thoroughly washed out with the 25 ml. of H<sub>2</sub>SO<sub>4</sub>, so that none of the sample is lost. The determination in the nitrometer is completed in the usual manner, the result being expressed as percentage of nitrogen in the dried sample of nitrocellulose.

### NITROGEN BY FERROUS-TITANOUS TITRATION

Alternatively, the nitrogen content of nitrocellulose may be determined by the ferrous-titanous titrimetric procedure. A dry sample of the nitrocellulose is transferred from a small weighing bottle to the special reduction flask by means of a powder funnel and a stream of *n*-pentane-*n*-hexane solvent (3:1) from an all-glass or polyethylene wash bottle. The determination is then continued in accordance with the detailed procedure given under "Nitrocellulose by Ferrous-Titanous Titration," p. 1390.

$$\text{Nitrogen, per cent} = \frac{0.4669N(V - B)}{W} \quad (\text{See Eq. 32-1.})$$

### SOLUBILITY IN ETHER-ALCOHOL

#### GUNCOTTON: SOLUBILITY BY USUAL GRAVIMETRIC PROCEDURE

The amount of ether-alcohol soluble material in guncotton being usually not more than 10 to 12%, the determination may be made by evaporating a clear solution.

*Procedure.*—Two g. of air-dry sample are placed in a clean, dry, cork-stoppered, 250-ml. cylinder, and 67 ml. of 95% ethyl alcohol are added to wet the guncotton thoroughly. Then 133 ml. of diethyl ether (U.S.P. grade 96%) are added and the mixture is well shaken. If the mixture of 2 parts ether and 1 part alcohol be added at once to the sample, a gummy mass may result that dissolves with great difficulty, especially if the solubility is unusually high.

The cylinder is now allowed to stand at a constant temperature of usually 15.5°C. The solubility of nitrocellulose *increases* as the temperature is decreased; hence, a constant temperature of digestion is important. During the digestion, which requires at least 1 hr., the cylinder must be thoroughly shaken at 5-min. intervals. The cylinder is then allowed to stand for at least 4 hr., until the insoluble portion of the sample has completely settled, and the supernatant liquid is perfectly clear.

Fifty ml. of the clear solution are now drawn off with a pipet, care being taken not to disturb the settled pulp, and evaporated in a weighed evaporating dish on a steam bath, avoiding loss from violent boiling of the ether. When 25 to 30% of the solution has been evaporated, 10 ml. of distilled water are added slowly, and the evaporation is continued to dryness. The effect of the water is to leave the residue in a white, brittle, or powdery condition, rather than a tough film, which would lose its solvent with difficulty.

The dish is finally placed in an oven at 95° to 100°C. for 30 min., cooled in a desiccator, and weighed. The weight of the residue, corrected for the residue in the 50 ml. of ether-alcohol and 10 ml. H<sub>2</sub>O used, represents the soluble nitrocellulose in 0.5 g. of the guncotton.

$$\text{Ether-alcohol soluble nitrocellulose, per cent} = \frac{225(W_2 - W_1)}{W_0}$$

where  $W_2$  = weight of can, cover, and residue in grams,

$W_1$  = weight of can and cover in grams, and

$W_0$  = total weight of sample taken for treatment in the solubility tube in grams.

**Gravimetric Method Using the Centrifuge.**—An accurately weighed dry sample of 0.3 g. is treated in a 150-ml. beaker with 45 ml. of 2:1 ether-alcohol mixture, and allowed to stand overnight under a bell jar. The solution is transferred to a 100-ml. centrifuge tube, using ether-alcohol as a transfer liquid, and is made up to the 100-ml. mark with this liquid. The tube is centrifuged at 2000 r.p.m. for 10 min. The supernatant liquid is decanted, the tube refilled with ether-alcohol mixture, shaken, and centrifuged. This cycle of decantation, refilling, and centrifuging, is repeated 2 more times (total of 4). After the final decantation, the residue of insoluble matter is transferred to a tared filtering crucible and washed with 2:1 ether-alcohol. The crucible is dried by suction, until ether-free, then at 100°C. for 30 min., cooled, and weighed.

$$\text{Ether-alcohol soluble nitrocellulose, per cent} = 100 \left[ 1 - \left( \frac{W_2 - W_1}{W_0} \right) \right]$$

where  $W_2$  = weight of crucible and residue in grams,

$W_1$  = weight of crucible in grams, and

$W_0$  = weight of sample taken originally for treatment in the centrifuge tube in grams.

### SOLUBILITY IN ACETONE

**Procedure.**—A 1-g. sample of air-dry pyrocellulose in a 300-ml. Erlenmeyer flask is moistened with 10 ml. of 95% ethanol, and then treated with about 200 ml. of acetone, with frequent shaking, until all gelatinous matter has dissolved. The solution is transferred to a solubility tube (described above, p. 1332), is shaken well, and allowed to settle for about 16 hr. If the volumetric reading is 0.2 ml. or less, the percentage of insoluble material is considered to be 0.4% or less. A gravimetric determination may be made as described above, under "Pyrocellulose," p. 1332.

### ASH

**Procedure.**—A 2-g. air-dry sample is weighed in a tared crucible, moistened with 10 to 15 drops of concentrated  $\text{HNO}_3$ , and digested for 2 to 3 hr. on a steam bath until converted to a gummy mass. The crucible is then heated carefully over a small burner until the mass is completely charred, then at a red heat over a Meker burner until its weight is constant. The residue is the ash of the sample.

### STABILITY TEST: HEAT TEST WITH POTASSIUM IODIDE-STARCH PAPER

The heat test with potassium iodide-starch paper is the test most frequently employed for determining the stability or degree of purification of nitrocellulose, whether guncotton or pyrocellulose. This test, also referred to as the Abel test, depends on the action of oxides of nitrogen evolved from the nitrocellulose under

papers at 5-min. intervals after the first 20 min. of heating, and replaced at once. The time required for the methyl violet paper in at least one tube to become completely changed to a salmon pink color is noted as the time of the test. A minimum test of 30 min. is usually required, and heating is then continued for a total of 5 hr., during which time there should be no explosion.

The standard, normal, methyl violet paper is usually obtained from the U. S. Naval Propellants Plant, Indianhead, Maryland, or is supplied by the government bureau or agency concerned.

## NITROGLYCERIN (GLYCERYL TRINITRATE)

### MOISTURE

Moisture in nitroglycerin is determined by a desiccation method or, preferably, by the Karl Fischer titration.

**Desiccation Procedure.**—A weighed sample of approximately 10 g. in a tared weighing dish of about 50-mm. diameter, which contains a small piece of neutral litmus paper, is allowed to stand for at least 16 hr., in a desiccator containing anhydrous calcium chloride, and is then reweighed. Loss in weight is calculated to percentage of moisture in the sample. **Caution.**—If the litmus paper turns red at any time during the test, immediately and cautiously dispose of the sample by drowning it in water or dibutyl phthalate.

**Karl Fischer Titration Procedure.**—A 5- to 10-g. sample is added to 50 ml. of methanol that has been brought to equilibrium in the titration cell, and is titrated by the usual potentiometric procedure, either directly with standard Karl Fischer reagent or by back-titration of a measured excess of Karl Fischer reagent with standard water-in-methanol solution (see p. 1290).

### ACIDITY OR ALKALINITY

**Procedure.**—A weighed sample of approximately 10 g. is dissolved in 100 ml. of benzene in a beaker. The solution is transferred to a 250-ml. separatory funnel, and washed twice with 50-ml. portions of neutral distilled water. The combined washings are collected in a 250-ml. beaker. Several drops of methyl orange indicator are added, and the solution is titrated with 0.01 *N* H<sub>2</sub>SO<sub>4</sub> or 0.01 *N* NaOH, as appropriate. A blank determination is made on 100 ml. of the benzene.

$$\text{Acidity in terms of sulfuric acid, per cent} = \frac{4.90N(V - B)}{W}$$

or

$$\text{Alkalinity in terms of sodium carbonate, per cent} = \frac{5.30N(V - B)}{W}$$

(See Eq. 32-1.)

### PERCENTAGE OF NITROGEN BY NITROMETER

**Procedure.**—A dry sample of 0.70 to 0.75 g. of the nitroglycerin is dissolved in 5 ml. of glacial acetic acid in a 25-ml. beaker. The solution is transferred with the aid of a small glass rod to the cup of the generating bulb of the nitrometer, and drawn into the generating bulb. The beaker and cup are rinsed with five 5-ml. portions of 94.5 ± 0.5% H<sub>2</sub>SO<sub>4</sub>, drawing each portion into the generating bulb.



The determination is then completed in the usual way (Vol I p 755). Joint Army Navy specification JAN N 246 requires that preparation of the sample be by suction filtration through 4 dry No 42 Whatman (or equivalent) filter papers; it applies the following calculations for a moisture free basis. (The papers are dried before use by heating in a dish for 2 hr in an oven at 100°C)

$$\text{Nitrogen (N) per cent} = \frac{A}{0.9983W}$$

where  $A$  = the reading of the mercury level in the nitrometer tube,

$W$  = weight of the filtered sample taken for analysis in grams, and 0.9983 is a recovery factor based on the experimentally determined average moisture content of nitroglycerin subjected to the prescribed filtration treatment

### STABILITY TEST WITH POTASSIUM IODIDE STARCH PAPER AT 82.2°C

*Procedure*—Filter a portion of the sample through 2 thicknesses of filter paper and transfer a 2 ml portion to each of three 5½ in test tubes, and continue the test as described for "Stability Test Heat Test with Potassium Iodide Starch Paper," p 1333

### NITROGUANIDINE (PICRITE)

#### ASSAY

The assay for nitroguanidine  $\text{NO}_2\text{NHC(NH)NH}_2$ , is made by the conventional nitrometer method (Vol I, p 755) on a sample that has been dried at 98° to 102°C. It may, alternatively, be made by the titanous chloride buffer method as described under Nitroguanidine by Buffered Titanous Chloride Reduction p 1394

#### ASH

*Procedure*—A 5 g sample of the nitroguanidine and 15 ml of melted paraffin wax are ignited (behind a shatterproof safety shield) in a tared crucible, using a low flame from a Bunsen burner directed only toward the bottom of the crucible. The crucible is finally ignited at 900°C. A blank determination is made on the paraffin wax, and a suitable correction applied to the calculation of the percentage of ash

#### CHLORIDES

Chlorides are determined by the Volhard silver nitrate procedure, on a boiling water extract from a 10 g sample (see p 1312)

$$\text{Sodium chloride, NaCl, per cent} = \frac{5.846(A'N - B'N')}{W} \quad (\text{See Eq 32-4})$$

#### TOTAL VOLATILES

Loss in weight of a 5 g sample at 100° ± 2°C for 2 hr is calculated to percent age of total volatiles

#### SULFATES

Sulfates are determined by the conventional gravimetric  $\text{BaSO}_4$  procedure on a hot water extract of a 5 g sample  $\text{BaSO}_4 \times 0.6086 = \text{Na}_2\text{SO}_4$

## WATER-INSOLUBLE IMPURITIES

Water-insoluble impurities are determined by filtering a boiling water extract of a 5-g. sample through a tared filtering crucible and weighing the insoluble material.

## WATER-SOLUBLE IMPURITIES

*Procedure.*—A 5-g. sample is shaken for 1 min. with 100 ml. of distilled water at room temperature in a stoppered 150-ml. bottle. The bottle is then held in a water bath at  $20^{\circ} \pm 0.2^{\circ}\text{C}$ . for 4 hr. with occasional withdrawals from the bath and shaking. A 20-ml. filtered aliquot is evaporated in a tared flask at a temperature not above  $60^{\circ}\text{C}$ . with the aid of a dry air jet. The flask is finally dried over calcium chloride in a desiccator to constant weight. A correction of 0.054 g. per gram of sample is deducted (for solubility of nitroguanidine) in making the calculation to percentage of water-soluble impurities.

## ACIDITY

*Procedure.*—A 2.5-g. sample is maintained at  $80^{\circ} \pm 2^{\circ}\text{C}$ . with 100 ml. of freshly boiled distilled water in a flask until solution is complete. After cooling, the solution is titrated with 0.05 *N* NaOH using phenolphthalein as indicator. A blank is also made.

$$\text{Acidity (as H}_2\text{SO}_4\text{), per cent} = \frac{4.9N(V - B)}{W} \quad (\text{See Eq. 32-1.})$$

*pH.*—The pH of an aqueous extract prepared at  $80^{\circ} \pm 2^{\circ}\text{C}$ . is measured at room temperature with a pH meter and glass-calomel electrode system.

## POLYPROPYLENE GLYCOL

## WATER

Determine water by the Karl Fischer titration as described above, p. 1290.

## VOLATILITY

*Procedure.*—Transfer approximately 250 ml. of the sample to a dry, tared, 500-ml., common, distillation flask, e.g., Corning Glass Works item No. 4620 (weighed to the nearest 0.1 g.) equipped with a  $-20^{\circ}$  to  $150^{\circ}\text{C}$ . thermometer [ASTM-E-1 (1C-49)], which is immersed in the sample, and containing a covered magnetic stirring bar; reweigh to the nearest 0.02 g. on a torsion balance of adequate capacity. Place the flask in a suitable heating mantle, and connect the side arm of the flask to a source of vacuum through a cold trap. Stir the contents of the flask throughout the volatility determination. Slowly reduce the pressure in the flask to approximately 10 mm. Hg, and gradually raise the temperature of the contents to  $150^{\circ}\text{C}$ . within 20 min., and then maintain the contents of the flask at  $150^{\circ} \pm 1^{\circ}\text{C}$ . for 10 min. by adjustments of the current supplied to the heating mantle. At all times, maintain the pressure at  $10 \pm 1$  mm. Hg absolute by a manostat or a nitrogen leak. Remove the heating mantle and allow the contents of the flask to return slowly to room temperature while maintaining 10 mm. of pressure. When the contents are cool, allow the pressure in the flask to come slowly to equilibrium with the atmosphere. Reweigh the flask assembly and contents to the nearest 0.02 g. Cal-

level of liquid in the bottles is below the water level in the bath; maintain the temperature of the bath at  $98^{\circ} \pm 2^{\circ}\text{C}$ . To ensure uniform heating of blanks and samples, place them as close together as possible. Because the bottles may explode, enclose each in a strong canvas bag, or erect a safety shield. After a reaction time of 120 min., remove the bottles and allow them to cool in air to room temperature. If fabric bags are employed, allow the bottles to cool, open the bags, carefully uncap the bottles to release any pressure, and then remove the bags.

To each of the bottles add 50.00 ml. of standard 0.5 *N* NaOH solution, then add 5 drops of 1% w/v phenolphthalein-in-pyridine indicator, and titrate with 0.5 *N* NaOH solution to a faint pink end point that persists for at least 15 sec.

$$\text{Hydroxyl content, milliequivalents per gram} = \frac{N(B - S)}{W} + A$$

where the symbols have the same meanings as those given above under "Acetylation Procedure."

### UNSATURATION

**Reagent.**—Prepare 0.10 *M* mercuric acetate alcoholic solution as follows: dissolve 32 g. of reagent-grade mercuric acetate and 2 to 3 drops of glacial acetic acid in sufficient anhydrous methanol to make 1 liter of solution; the reagent should be slightly acidic, i.e., a blank titration of 2 to 4 ml. of 0.05 *N* alcoholic KOH should be required; decant the reagent before using. Prepare the solution weekly; do not use it if an orange precipitate has formed.

**Procedure.**—Pipet 50.00 ml. of 0.10 *M* mercuric acetate solution into 250-ml., glass-stoppered Erlenmeyer flasks for blank and sample determinations. Introduce a 30-g. portion of the sample (weighed to the nearest 0.1 g.) into each of the sample flasks, and mix well by swirling. Allow the samples and blanks to stand at room temperature for 30 min. Swirl the flasks several times during this period. To each flask add 6 to 8 g. of reagent-grade NaBr, and swirl vigorously. Add approximately 1 ml. of a 1.0% w/v alcoholic solution of phenolphthalein indicator, and immediately titrate with a standard 0.05 *N* alcoholic KOH solution to a faint pink end point that persists for 15 sec. One of the blank titrations should be carried out first; the other blank should be performed after all the samples have been titrated; the 2 blank values should be averaged.

$$\text{Unsaturation, milliequivalents per gram} = \frac{N(S - B)}{W} - A$$

where *N* = normality of the standard alcoholic KOH solution,

*S* = standard alcoholic KOH required by the sample in milliliters,

*B* = standard alcoholic KOH required by the blank in milliliters (average),

*W* = weight of sample taken for analysis in grams, and

*A* = acidity of sample in milliequivalents per gram.

### 2,4-TOLUENE DIISOCYANATE

#### ASSAY

**Reagent.**—Prepare dry toluene by careful distillation of reagent-grade material; reject the first third of the distillate as it will contain all of the water in the start-

ing material Prepare a 2 *N* solution of di *n* butylamine by diluting 250 g of the redistilled amine with dry toluene to make a total of 1 liter Store the solution in an automatic buret protected from ingress of moisture by drying tubes that contain magnesium perchlorate

**Procedure** Dry a clean 250 ml Erlenmeyer flask and a bottle equipped with a ground glass dropper at 110°C and cool in a desiccator Transfer a small amount of the sample to the dropping bottle and attach a dry rubber bulb to the dropper Tare the dropping bottle and then transfer as quickly as possible 1.8 to 2.2 g of the sample (1.5 to 1.8 ml) to the 250 ml Erlenmeyer flask Immediately place the flask in an ice water bath and add exactly 50 ml of 2 *N* di *n* butylamine solution from a dispensing buret protected from ingress of moisture exercise caution because an exothermic reaction occurs Swirl the flask to mix the contents and then loosely stopper it

Reweigh the dropping bottle and determine the weight of sample transferred (nearest 0.2 mg) Remove the flask from the ice bath and allow the contents to come to room temperature (about 15 min) Add 100 ml of acetone and pour the contents of the flask into a 600 ml beaker use 200 ml of acetone to effect quantitative transfer of the flask's contents to the beaker Add 50 ml of distilled water and titrate with standard 1.0 *N* HCl to a pH of 4.0 using a pH meter or 0.5 ml of bromphenol blue indicator solution (prepared by mixing 0.10 g indicator powder with 15 ml of 1 *N* NaOH and diluting to 100 ml with water) Make a blank determination

$$\text{TDI per cent} = \frac{8.708N(B - A)}{W} \quad (\text{See Eq. 32-3})$$

### HYDROLYZABLE CHLORIDE

For hydrolyzable chloride content of about 0.005% use a 30 g sample for content of about 0.01% use a 15 g sample and for content of about 0.1% use a 3 g sample

**Procedure**—Place the sample directly in a 600 ml beaker and add 50 ml of reagent grade methanol (hood) When the reaction starts (usually within 30 sec) add 200 ml of distilled water and stir vigorously Cover the beaker with a watch glass and bring the solution to a boil allow boiling to continue for 20 min Cool the solution by immersion of the beaker in cold water

Filter the solution through paper of medium retentiveness into a 500 ml Erlenmeyer flask and wash the precipitate 3 times with distilled water Add 15 ml of 1.1 *N* HNO<sub>3</sub> and mix well Using standard 0.05 *N* AgNO<sub>3</sub> as titrant complete the determination of chloride by the conventional Volhard procedure or potentiometrically with a silver indicator electrode system

$$\text{Hydrolyzable chloride (Cl), per cent} = \frac{3.55(AV - BN)}{W} \quad (\text{See Eq. 32-4})$$

### TRIACETIN (GLYCERYL TRIACETATE)

#### ACIDITY

**Procedure**—Accurately measure 100 ml of sample into an Erlenmeyer flask Prepare 400 ml of neutralized 95% ethanol by titrating it to a faint pink color with 0.1 *N* standard NaOH solution, using 20 drops of 1% phenolphthalein as indicator

Add 200 ml. of the neutralized alcohol to the sample, mix thoroughly, and titrate rapidly with 0.1 *N* NaOH solution to a pink matching that of the remaining alcohol, disregarding gradual fading of the pink color.

$$\text{Acetic acid, per cent} = \frac{6.0NV}{W} \quad (\text{See Eq. 32-2.})$$

### ASH

*Procedure.*—Evaporate a 10-g. sample in a tared, covered, porcelain crucible by heating over a low flame or on a hot plate, with the cover of the crucible tilted to permit escape of vapors. Finally, ignite to constant weight at  $800^{\circ} \pm 50^{\circ}\text{C.}$ , cool, and reweigh.

### ESTER CONTENT (AS GLYCERYL TRIACETATE)

*Procedure.*—Using a weighing pipet (triacetin is hygroscopic) transfer an accurately weighed sample of 1.6 to 2.0 g. to a 250-ml. flask having an ST neck. Add exactly 100.0 ml. of 0.33 *N* aqueous standard NaOH solution (carbonate-free), connect the flask to a reflux condenser, and boil gently for 1 hr. with occasional swirling of the flask. Loosen the flask-condenser joint, and wash down the condenser and the joint by adding 25 ml. of distilled water through the top of the condenser. Cool the flask rapidly to room temperature using a cold water bath, disconnect it from the condenser, and titrate its contents with 0.3 *N* standard  $\text{H}_2\text{SO}_4$  solution using 10 drops of 1% phenolphthalein as indicator. Make a blank determination on exactly 100.0 ml. of the standard NaOH solution.

$$\text{Glyceryl triacetate, per cent} = \frac{7.27N(B - A)}{W} \quad (\text{See Eq. 32-3.})$$

### 2,4,6-TRINITROTOLUENE (TNT)

#### SOLIDIFICATION POINT

The determination of the solidification point or "setting point" of TNT is commonly used as a test for purity of this compound, and is preferably carried out as follows.

*Procedure.*—A sample of about 50 g. of TNT is placed in a 1 by 6 in. test tube, and melted by placing the tube in an oven at about  $95^{\circ}\text{C.}$  The tube is then inserted through a large cork stopper into a larger test tube about  $1\frac{1}{2}$  by 7 in., which, in turn, is lowered through a cork into a wide-mouth liter bottle (see Fig. 32-10). The inner test tube is provided with a cork stopper containing 3 openings: 1 for a standard total-immersion thermometer, graduated in  $0.05^{\circ}\text{C.}$ ; 1 for a short thermometer, with  $1^{\circ}\text{C.}$  subdivisions, that is passed just through the stopper; and 1, a small v-shaped notch at the side of the stopper, through which passes a rod whose lower end is bent in a loop at right angles to the axis of the tube. The short thermometer is used for noting the average temperature of the exposed mercury column of the standard thermometer. The rod with loop is used for stirring the molten sample of TNT. The stirring rod may be made of glass, brass, or aluminum.

The standard thermometer is so adjusted that its bulb is in the center of the molten mass. The stirrer is operated vigorously, and the thermometer is watched

carefully as the temperature falls. The temperature will finally remain constant for an appreciable time and then rise slightly, because of the heat of crystallization of the TNT. As this period is reached readings should be taken about every 15 sec until the maximum temperature of the rise is noted. The temperature will usually remain constant for several minutes while crystallization is proceeding. The maximum reading corrected for the emergent stem of the thermometer, is

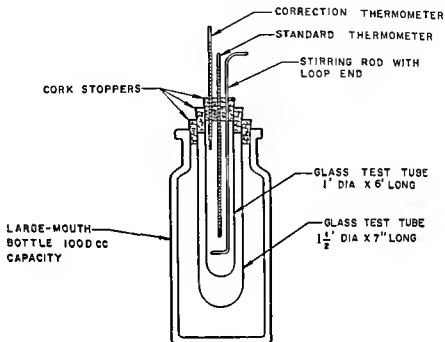


FIG. 32-10 Solidification Point Apparatus

taken as the solidification point of the sample. The emergent stem correction is calculated as follows and added to the observed reading

$$\text{Correction, in degrees Centigrade} = N(T - t)(0.000158)$$

where  $N$  = number of degrees on the standard thermometer that are emergent from the bath,

$T$  = uncorrected solidification point, and

$t$  = average temperature of the exposed mercury column read on the auxiliary thermometer with its bulb at the midpoint of the exposed mercury column

### MOISTURE

**Procedure.**—A sample of 5 to 6 g is dried in a vacuum desiccator containing indicating Drierite indicating silica gel, or fresh anhydrous calcium chloride, for 30 min at an absolute pressure of 100 to 360 mm of mercury. Loss in weight is calculated to percentage of moisture.

### INSOLUBLE

**Procedure.**—A sample of about 10 g is treated with 150 ml of benzene heated to boiling, and filtered while hot through a tared Gooch crucible with asbestos mat

The insoluble residue is washed with additional solvent, dried at 100°C., and weighed.

### ACIDITY

*Procedure.*—A 10-g. sample is melted in a large test tube or a flask, shaken with 100 ml. of neutralized boiling water, cooled, and the water is decanted. A similar treatment is given, using 50 ml. of boiling water, the 2 portions of water combined, cooled, and titrated with 0.05 *N* NaOH, using cresol red indicator. The acidity is calculated as percentage of  $\text{H}_2\text{SO}_4$  in the original sample.

### ALKALINITY

Bromthymol blue indicator solution is added to an aqueous extract obtained by extracting a sample in the manner used for the acidity determination. The sample is considered unsatisfactory if a definite alkaline color reaction is produced.

### SODIUM

*Procedure.*—A 10-g. sample of sodium-free TNT is transferred to a  $\frac{7}{8}$  by 6 in. test tube. Fifteen ml. of sodium carbonate solution, containing 0.0154 g.  $\text{Na}_2\text{CO}_3$  per liter (equivalent to 0.001% Na for a 10-g. sample of TNT), are added to the test tube. A 10-g. sample of the TNT to be tested and 15 ml. of water are added to a similar test tube. Both tubes are heated in a boiling water bath for 30 min. with continuous agitation or vigorous shaking at 2-min. intervals. After cooling, the water extracts are decanted into 50-ml. Nessler tubes. The residue in each test tube is rinsed with 10 ml. of distilled water, the washings being added to the original extracts in the Nessler tubes. Fifteen ml. of reagent-grade acetone and 1 ml. of 8% w/v oxalic acid solution are added to each Nessler tube. The tubes are shaken thoroughly, the liquid volumes are made to 50 ml., and the tube contents are again mixed. After standing 10 min., the colors of the solutions are compared. If the color of the solution from the tested sample is definitely less than that from the standard, the sample is satisfactory. If the color of the sample solution is equal to or darker than the standard, sodium is determined gravimetrically by the magnesium uranyl acetate method.

### NITROGEN

Nitrogen is not usually determined in the inspection of TNT, but, when necessary, it may be determined by the Dumas combustion method or the modification of the Kjeldahl method that uses salicylic and sulfuric acids in a preliminary digestion followed by the usual digestion with  $\text{HgO}$ ,  $\text{K}_2\text{SO}_4$ , and  $\text{H}_2\text{SO}_4$ , and by distillation as described under "Kjeldahl-Gunning-Arnold Method." (See Vol. I, p. 740.)

### ZINC OXIDE

#### ZINC OXIDE ASSAY

This determination is made by titration with 0.1 *M* disodium ethylenediamine-tetraacetate (EDTA).

*Reagents.* **Buffer Solution.**—This solution consists of 54 g.  $\text{NH}_4\text{Cl}$  and 350 ml. of  $\text{NH}_4\text{OH}$  made up to 1000 ml. with distilled water.

# EXPLOSIVES

The quantitative procedures for the analysis of single explosive materials such as nitroglycerin and nitrocellulose (for assay and for impurities) are presented in the "Ingredients" section, above, p. 1306. Qualitative tests, quoted with slight modifications from the work cited in footnote 1, are given below, and additional qualitative tests are described in conjunction with the quantitative analysis of dynamites. Some valuable qualitative techniques are also described in an article by Walter C. McCrone.<sup>19</sup>

## QUALITATIVE TESTS OF EXPLOSIVES<sup>20</sup>

Before making any specific tests for identity, the unknown material should be examined for color, density, and sensitivity to flame, impact, and friction. The sensitivity tests may be made by subjecting a few small particles of the material to the flame of a match, to impact, and to rubbing with a steel hammer, the material being placed on a steel block or hammer. Black powder flashes when exposed to a flame, but does not explode when struck lightly or rubbed with a hammer. Initiating explosives explode or flash when in contact with a flame, and explode when struck or rubbed with a hammer. Solid noninitiating explosives burn without explosion, and are much less sensitive than the initiators to impact and friction.

Visual comparison of the color and crystal structure of the unknown material with the characteristics of standard explosives shown in paragraphs 40 through 67 of *Military Explosives*, will be of assistance in tentative identification. Should an unknown explosive be indicated to be of the sensitive type, special care should be taken in the removal of test samples, handling, and heating. Dense pressed pellets of explosive found to be, or suspected of being, sensitive, should be softened by soaking with water or alcohol, prior to the removal of test samples. Care should be taken also regarding possible ignition by static electricity, because some materials are extremely sensitive to static sparks.

## INITIATING EXPLOSIVES

### LEAD AZIDE

**Procedure.**—Test the explosive for solubility in water. Lead azide is insoluble in water.

Transfer 5 mg. of the sample explosive to a 10-ml. beaker and add 10 drops of

<sup>19</sup> The Identification of High Explosives by Microscopic Fusion Methods, *Microchemical Journal*, 3, 479, Nov., 1959.

<sup>20</sup> Beginning with the following paragraph and concluding on p. 1350, material is quoted directly from *Military Explosives*, footnote 1, with only minor modifications. It is reproduced by permission of the Department of the Army. The contents of Table 32-2 are also essentially verbatim from that reference.



a 10% ceric ammonium nitrate solution. A reaction accompanied by evolution of nitrogen gas is indicative of the presence of azide.

Treat the solution of the sample obtained in the preceding paragraph with a few drops of a 10% solution of potassium dichromate. A yellow to reddish yellow precipitate is indicative of the presence of lead.

Transfer 2 mg of the sample to a 30 ml beaker. Add 5 ml of a 10% solution of ferric chloride solution. A red color is formed which disappears slowly when a few milliliters of dilute mercuric chloride solution are added. This confirms that the explosive is lead azide.

#### MERCURY FULMINATE

*Procedure*—Test the explosive for solubility in water. Mercury fulminate is insoluble in water.

Transfer 10 mg of the sample explosive to a fritted glass crucible of medium porosity. Extract the sample with a 20% solution of sodium thiosulfate, catching the washings in a 50 ml beaker containing 10 drops of a 1% phenolphthalein indicator solution. When the mercury fulminate is treated with sodium thiosulfate it dissolves with formation of alkali (NaOH) which changes the color of the indicator solution from colorless to red.

Transfer 10 mg of the sample to a 10 ml beaker and add 3 drops of concentrated HCl solution and 2 ml of water. Transfer the solution to another beaker containing 1 drop of a 5% solution of potassium iodide. The formation of a bright red precipitate indicates the presence of the mercuric ion.

#### DIAZODINITROPHENOL (DDNP)

*Procedure*—Dissolve 0.05 g of the low density greenish yellow to brown explosive in acetone. Upon adding a larger volume of ice water the explosive should appear as a bright yellow precipitate. Prepare a saturated solution of the explosive in 200 ml of water. Add to this 5 ml of a 20% solution of NaOH and mix. The evolution of a colorless gas and the appearance of a reddish brown color in the solution indicate the explosive to be diazodinitrophenol.

#### LEAD STYPHNATE

*Procedure*—Wet 0.1 g of the heavy light orange to reddish brown material with 10 ml of water and then add slowly 10 ml of a 20% solution of ammonium acetate. Agitate the mixture until solution is complete. Add 10 ml of a 10% solution of potassium dichromate. The appearance of a bright yellow precipitate indicates the presence of lead. To 0.1 g of the explosive in a beaker add 10 ml of a 10% solution of HCl. Heat the mixture on a steam bath and evaporate to dryness. Cool the beaker and contents and add 10 ml of diethyl ether. Mix the contents and allow to settle. Decant or filter off the ether solution and evaporate it to dryness at room temperature. Dissolve the residue in 25 ml of water and add 0.1 g of solid KCN. The absence of color indicates the explosive to be lead stypnate.

#### TETRACENE

*Procedure*—Wet 0.25 g of the fluffy pale yellow explosive with 5 ml of a 10% solution of NaOH and warm the mixture on a steam bath until solution is complete. Note if there is an odor of ammonia. Cool the solution and add 1 ml

of a 5% solution of copper acetate. The appearance of a bright blue precipitate indicates the explosive to be tetracene. If 0.25 g. of the unknown explosive is not available, the identification could be carried out microscopically.

## NONINITIATING EXPLOSIVES

### GENERAL TESTS

Many noninitiating explosives can be identified by making a series of tests, and comparing the results with those given in Table 32-2. The tests are as indicated below.

**Test 1.**—Place 0.05 g. of the explosive in a 5-ml. beaker, add 2 to 3 ml. of distilled water, and stir for 5 min. Observe the color of the liquid. Wet one end of a strip of universal pH indicator paper, and note any change in color. Add a drop of Nessler's reagent and note the color of any precipitate formed. Prepare the reagent by dissolving 5 g. of potassium iodide in a minimum quantity of cold distilled water, and adding a saturated aqueous solution of mercuric iodide until a faint precipitate is formed. Add 40 ml. of 50% potassium hydroxide solution. After the solution has clarified by settling, dilute to 100 ml. with distilled water, allow to settle, and decant.

**Test 2.**—Place 0.05 g. of the unknown material in an indenture of a white porcelain spot-test plate. Add 2 or 3 drops of a 65 to 68% aqueous solution of ethylenediamine, and stir. Note the color of the solution (not the solid).

**Test 3.**—Place 0.05 g. of the unknown material in an indenture of a white porcelain spot-test plate, and add 3 or 4 drops of a diphenylamine solution. Stir the mixture and, after 1 min., note the color of the solution. Prepare the diphenylamine solution by dissolving 1 g. of diphenylamine in 100 ml. of concentrated reagent-grade sulfuric acid.

**Test 4.**—Place 0.05 g. of the unknown material in an indenture of a white porcelain spot-test plate. Add an equal amount of crystalline thymol and 3 drops of concentrated sulfuric acid. Stir the mixture and note its color after 5 min. or more.

### AUXILIARY TESTS FOR SPECIFIC MATERIALS

**RDX.**—Place 1 ml. of the white, unknown material in an indenture of a white porcelain spot-test plate, and add not more than 1 ml. of thymol. Grind and mix the 2 materials intimately with the end of a glass stirring rod. Add 3 drops of concentrated  $\text{H}_2\text{SO}_4$ , and stir. After 1 min., add 2 drops of 95% ethanol, and stir the mixture. The appearance of a pink or rose color indicates the presence of RDX. If a blank test is made, a faint pink color is developed, but the effect of the presence of RDX is unmistakable.

**Composition A-3.**—Place 0.1 g. of the material in a 10-ml. beaker and add 2 or 3 drops of acetone. Warm the mixture and allow to stand for 5 min. Evaporate the acetone by gently warming on a steam bath, cool, and add 2 ml. of carbon tetrachloride. Cover the beaker and warm the contents, occasionally swirling the mixture. Cool the mixture and allow the undissolved material to settle. Decant the supernatant liquid into a 5-ml. beaker, evaporate to dryness, and note if a waxy (not tarry) residue is obtained. Dry the undissolved material in the 10-ml. beaker, and test for RDX as described above.

**Composition B.**—Place 0.2 g. of the pale yellow to medium brown material in a 10-ml. beaker, and add 2 to 3 ml. of chloroform. Cover the beaker. Warm and

TABLE 32-2 TESTS OF NONINITIATING EXPLOSIVES

	Water Solution or Extract			Color Effect of Test		
	Color	Color of Universal pH Test	Color of Precipitate with Nessler's	Ethylene diamine	Diphenyl amine	Thymol
TNT	(Insoluble)			Maroon	Colorless	
Tetryl	(Insoluble)			Red	Blue	Green
Picric acid	Yellow	Red	No precipitate	Orange		
Explosive D	Yellow		Brown	Orange		
Halite	None		No precipitate	None	Blue *	Orange
Nitroguanidine	None		White		Blue	Green
Ammonium nitrate	None		Brown	None	Dirty green	Green *
PETN	(Insoluble)			None	Dirty green	Green
Nitroglycerin	None		No precipitate		Deep blue	Green
DEGN	None		No precipitate		Deep blue	Brown <sup>b</sup>
Nitrocellulose	None				Blue	Green
Tritonal	(Insoluble)			Maroon	Colorless	
Tetrytol	(Insoluble)		No precipitate	Maroon	Intense blue	Green
Picratol	Yellow		Brown	Maroon		
Ednatol	None	Orange	No precipitate	Maroon	Intense blue	Orange
Amatol	None		Brown	Maroon	Dirty green	Green
Ammonal	None		Brown	Maroon	Dirty green	Green
Pentolite	None		No precipitate	Maroon	Dirty green	Green
Trimonite	Yellow	Red	No precipitate	Orange	Red	
Tridite	Yellow	Red	No precipitate	Orange		
Black powder <sup>c</sup>	None	No change			Blue	Green

\* Color appears immediately

<sup>b</sup> Sometimes explodes mildly (puffs) upon addition of sulfuric acid

<sup>c</sup> Tests of dried water extract

digest the mixture for 10 min with occasional swirling. Decant the supernatant liquid through a paper filter and evaporate the filtrate to dryness. Digest the insoluble residue in the beaker with 3 more portions of chloroform, discarding the decanted liquid in each case. Dry the insoluble residue by evaporating any adherent chloroform. If the original material was composition B, the residue from evaporation of the chloroform filtrate consists of TNT and wax. Test the TNT and wax mixture with ethylenediamine and diphenylamine as described in Test

2," and "Test 3" above (Table 32-2). The residue insoluble in chloroform consists of RDX. Test it as described above.

**Composition C-3.**—Place 0.2 g. of the putty-like explosive in a 10-ml. beaker, and add 5 ml. of benzene. Mix and digest for 10 min., crushing any lumps present. Decant the supernatant liquid through a paper filter, and evaporate the benzene with gentle heating. Note whether a dark, tarry residue remains. Wash the insoluble residue left by benzene extraction with two or three 3-ml. portions of a 2:1 ether-ethanol mixture, and dry the washed residue. Test this as described under "RDX," above. To the decanted ether-ethanol washings, add 15 ml. of distilled water, and heat the mixture until all ether and alcohol are removed. Note if a white precipitate separates; if so, it is nitrocellulose. Catch the precipitate on a filter, wash with ethanol, dry by evaporation of the ethanol, and test for nitrocellulose as described in "General Tests," above (Table 32-2).

**Torpex.**—Place 0.2 g. of the explosive in a 5-ml. beaker, and extract with three 3-ml. portions of acetone. Dry the insoluble residue, and examine it under a microscope. Note if it has the characteristic appearance of metallic aluminum. Place 0.2 g. of the explosive in a 5-ml. beaker, and digest with two 3-ml. portions of benzene, decanting the benzene into a small evaporating dish. Evaporate the benzene solution to dryness and test for TNT as described above (Table 32-2). Dry the insoluble residue from the benzene extraction and test for RDX as described above.

**Tritonal.**—Place 0.2 g. of the explosive in a 10-ml. beaker, and add 5 ml. of acetone. Stir, allow any undissolved material to settle, and decant the liquid. Wash the insoluble matter with two 5-ml. portions of acetone, dry, and examine under a microscope. Note if it has the characteristic appearance of metallic aluminum. Subject the explosive to the tests prescribed for TNT in Table 32-2.

**Amatol.**—Place 0.2 g. of the yellow material in a 5-ml. beaker, add 3 ml. of distilled water, and stir for 5 min. Decant the liquid through a filter, and evaporate to dryness. Test the dried solid as prescribed for ammonium nitrate (see Table 32-2). Dry the water-insoluble residue, and test as prescribed for TNT in Table 32-2.

**Ammonal.**—Place 0.2 g. of the explosive in a 10-ml. beaker, and digest with 3 ml. of distilled water. Decant the liquid through a filter, and evaporate to dryness. Test the dried solid as prescribed for ammonium nitrate (see Table 32-2). Digest the insoluble residue in the beaker with three 3-ml. portions of acetone, decanting these through a filter. Dry the insoluble residue, and examine it under a microscope. Note if it has the characteristic appearance of metallic aluminum. Evaporate the filtrate to dryness by warming gently. Test the dried solid as prescribed for TNT in Table 32-2.

### BLACK POWDER (INITIATING EXPLOSIVE AS USED AS AN IGNITER OR FUZE; NONINITIATING EXPLOSIVE AS USED FOR A BURSTING OR BLASTING CHARGE)

**Procedure.**—Place 0.2 g. of the black material in a 5-ml. beaker, add 2 to 3 ml. of distilled water, and stir for 5 min. Decant the liquid through a filter, and catch the filtrate in a beaker. Evaporate this to dryness, and subject the dried white solid to the tests shown in Table 32-2. Dry the water-insoluble residue in the beaker, cool, and digest with two 5-ml. portions of carbon disulfide, decanting

these into an evaporating dish. Evaporate the carbon disulfide solution to dryness at room temperature. By means of a microscope examine the yellow residue so obtained and the insoluble black residue from the carbon disulfide extraction. Note if they have the characteristic appearances of sulfur crystals and charcoal.

### WATER SOLUBLE SALTS

For the interpretation of results of analysis of an explosive mixture containing several water soluble salts it is frequently advantageous to determine the identity of one or more of the water soluble components. This may be done in a number of ways using a sample that has been freed from ether soluble constituents by solvent extraction. For example, the following techniques may be applied: microscopic examination, infrared spectrophotometry, X-ray diffraction, or mechanical separation based on differences in specific gravity, utilizing a series of test liquids of varying density prepared by mixing chloroform (sp. gr. 1.49) and bromoform (sp. gr. 2.83).

## QUANTITATIVE ANALYSIS OF EXPLOSIVE MIXTURES

A key to the quantitative analysis of common explosive mixtures is provided in Table 32.3.

Except for the Composition C formulations and dynamites all the explosives of Table 32.3 are readily analyzed by simple gravimetric procedures following extraction with a suitable solvent or a succession of solvents. A complete synopsis is not supplied here for Composition C formulations but suitable procedures will probably become apparent to the analyst when he examines the particular Composition C to be analyzed, and considers the solubility and chemical characteristics of each ingredient. Dynamite analysis is presented in the following section.

### DYNAMITES <sup>21</sup>

Alfred Nobel gave the name dynamite to the mixture of nitroglycerin and kieselguhr that he invented in 1866, the strength of the dynamite being indicated by the percentage of nitroglycerin in the mixture. The term is now applied to any solid blasting explosive that is a mixture of inorganic nitrate, carbonaceous material and an initiating compound (such as nitroglycerin).

By replacing the chemically inert kieselguhr with a combustible absorbent such as wood pulp and adding sodium nitrate, 'active dope' dynamites with improved explosive strength were produced. Later on by replacement of part of the nitroglycerin and sodium nitrate by ammonium nitrate less costly 'ammonia' dynamites were brought into existence. Over the last decade there has been a trend toward using higher and higher proportions of ammonium nitrate. Improvement in water resistance and plasticity, and increase in density were achieved by including nitrocellulose in dynamites to produce 'gelatin' dynamites. Blasting gelatins

<sup>21</sup> End of material quoted with minor modifications from Military Explosives.

<sup>22</sup> For a large proportion of the material presented under this heading the author is greatly indebted to Mr. W. W. Becker and others of the Hercules Research Center, Wilmington, Delaware; Mr. H. A. Read, of the Hercules Powder Company, Kent, New Jersey, and to technical personnel of the E. I. DuPont de Nemours and Company, Inc., especially Dr. W. F. Jackson of the Explosives Department, Research and Development Division, Wilmington, Delaware, and Mr. C. I. Johnson of the Eastern Laboratory, Gibbs town, New Jersey.

TABLE 32-3. EXPLOSIVE MIXTURES, QUANTITATIVE ANALYSIS OUTLINE <sup>a</sup>

Designation	Ingredients	Scheme of Analysis
Amatol Ammonal	TNT, $\text{NH}_4\text{NO}_3$ TNT, $\text{NH}_4\text{NO}_3$ , Al	Extract TNT in benzene. Extract TNT in $\text{C}_6\text{H}_6$ ; $\text{NH}_4\text{NO}_3$ in $\text{H}_2\text{O}$ .
Baratol Composition A (1, 3)	TNT, $\text{Ba}(\text{NO}_3)_2$ RDX, wax	Extract TNT in $\text{C}_6\text{H}_6$ . Extract wax in toluene (saturated with RDX).
Composition B	TNT, RDX, wax	Extract TNT and wax in toluene (saturated with RDX). <sup>b</sup>
Composition C (1, 2, 3, and 4)	TNT, RDX, plastic <sup>c</sup>	Extract TNT in toluene (saturated with RDX). <sup>d</sup>
Dynamites Nitroglycerin Straight Ammonia Gelatin Ammonia-Gelatin Low freezing Nitrostarch explosives "Permissible" explosives	See "Dynamites," p. 1350.	See "Dynamites," p. 1350.
Ednatol	TNT, EDNA	Extract TNT in dimethyl ether (saturated with EDNA).
Pentolite	TNT, PETN	Extract TNT in $\text{CHCl}_3$ (saturated with PETN).
Picratol	TNT, ammonium picrate	Extract TNT in cold di- ethyl ether (saturated with ammonium picrate).
Tetrytol	TNT, tetryl	Extract TNT in boiling $\text{CCl}_4$ , chill $0^\circ\text{C}$ . filter. Correct for solubility of tetryl in $0^\circ\text{C}$ . $\text{CCl}_4$ .
Torpex	TNT, RDX, Al	Extract TNT in toluene (saturated with RDX) and extract RDX in acetone leaving Al.
Tritonal	TNT, Al	Extract TNT in acetone.

<sup>a</sup> Based on Military Explosives, footnote 1.<sup>b</sup> Frequently percentage of TNT and wax are reported together. If separate values are needed, evaporate the toluene solvent to small volume, add 50 ml. of 70% acetic acid, boil, chill, filter out wax, dissolve wax in  $\text{CHCl}_3$ , and evaporate the  $\text{CHCl}_3$  solution in a tared beaker.<sup>c</sup> Plus small amounts of tetryl, polyisobutylene, nitrocellulose.<sup>d</sup> Remainder of the determination varies greatly depending on composition.

composed of 8 to 12% of nitrocellulose colloided with 88 to 92% of nitroglycerin are especially useful in underwater blasting

The cost of glycerin and the tendency of nitroglycerin to freeze at some atmospheric temperatures led to the partial replacement of nitroglycerin by antifreeze materials such as nitrated diglycerin dinitrotoluene and nitroglycol (ethylene glycol dinitrate). For economic reasons the last named material is the one most commonly used at present. Most of the currently used dynamites are of the low freezing type.

Nitrostarch explosives may contain in addition to the nitrostarch any of the following components: oxidizing agents such as sodium ammonium or calcium nitrate; combustible material such as aluminum flour sulfur paraffin or mineral oil; antacids such as calcium carbonate or zinc oxide; TNT, DNT, dicyandiamide, ferrosilicon and dyes. Nitrostarch dynamites are used in cartridge form with paper wrappers for commercial blasting.

Permissible explosives are coal mines explosives that have passed the prescribed tests by the Bureau of Mines and are approved by the Bureau on a trade name basis for use in underground coal mines. Bureau of Mines Information Circular 7832 shows that as of December 31, 1957, there were 159 different approved brands manufactured by eleven companies.<sup>23</sup>

The following analytical procedures apply to all classes of nitroglycerin dynamites (straight ammonium gelatin ammonium gelatin and low freezing) and to nitrostarch and permissible explosives. Table 32.4 shows typical compositions for 40% nitroglycerin dynamites.

TABLE 32.4 SOME TYPICAL DYNAMITE FORMULAS FOR "40%" GRADES, APPROXIMATE PERCENTAGE COMPOSITIONS ON DRY BASIS<sup>a</sup>

Type	NG	F P Depressants			NC	Carbonaceous Fuel (e.g. Wood Pulp)	Antacid (e.g., CaCO <sub>3</sub> )	S
		(e.g. DEGDN)	NH <sub>4</sub> NO <sub>3</sub>	NaNO <sub>3</sub>				
Straight	39	—	—	46	—	14	1	—
Ammonia	17	—	31	38	—	9	1	4
Gelatin	32	—	—	53	1	11	1	2
Ammonia Gelatin	26	—	8	51	0.5	8	1	55
Low Freezing	30	10	—	44	—	15	1	—
Low Freezing Ammonia	17	4	20	45	—	13	1	—

<sup>a</sup> Based on footnote 1, p. 206 and Bur. of Mines Bull. No. 80, p. 21.

Caution—(1) Use rubber gloves when sampling dynamite to avoid absorption of nitroglycerin by the skin. (2) Dispose of all waste materials in accordance with pertinent directions given in safety manuals on laboratory handling of explosives.

<sup>23</sup> Details of analysis are given in Storm, C. G. Bureau of Mines Bulletin No. 96, The Analysis of Permissible Explosives, 1916.

(3) Diethyl ether used for extractions must be free from peroxides (see instructions under "Procedure D-2. Ether Extraction," p. 1354 below).

### SAMPLE PREPARATION

Dynamites are subject to certain changes of composition, primarily because of segregation of the nitroglycerin in the lower portion, and secondarily, because of the greater absorption of moisture in the more exposed portion. These changes, especially those due to the primary cause, take place in a relatively short time; sticks of well-mixed dynamite, if allowed to stand on end for 24 hr., will show by analysis an appreciable difference in the nitroglycerin content of the upper and lower ends, the latter, of course, being the higher. With regard to the secondary cause, the ends of a cartridge are apt to show a higher moisture content than the middle portion, with a corresponding change in the general percentage composition. This is especially true when the shell crimps are not perfectly tight. Gelatin dynamites are much less subject to change from the two causes mentioned than other types of dynamite.

*Procedure.*—Carefully uncrimp the wrapper, and transfer the powder, in its original form, to a sheet of parchment paper or dynamite shell paper. Carefully remove and discard any traces of residual powder from each wrapper. Retain the cleaned wrapper for analysis. Take care that no paraffin from the wrapper, nor any adhering to the dynamite inside the ends of the cartridge, becomes mixed with the sample.

Using a spark-proof knife, cut off and discard about 1 in. of powder from each end of the stick. Thoroughly mix the remaining portion, preferably with a hard rubber spatula. Gelatin dynamites, after removal of the wrapper or shell, should be quartered lengthwise, cut into  $\frac{1}{4}$ -in. sections, and then blended.

The presence of any lumps of blasting gelatin should be reported for all types of dynamite examined.

Mix the sample and transfer it at once to a suitable wide-mouthed, rubber-stoppered bottle. Never use a glass stopper or a polyethylene container.

If portions of the dynamite for analysis are to be weighed out soon after sampling (within 1 hr.), the bottle may be kept on its side and the portion withdrawn without remixing; otherwise, it will be necessary to remix the sample just before taking any of it because of the settling of the nitroglycerin. In general, however, frequent remixing of a sample is to be avoided because of possible loss of nitroglycerin.

### COMPLETE ANALYSIS

Following qualitative testing, a typical complete analysis may take the form illustrated by the flow sheet of Fig. 32-II. (See Note on p. 1361.)

#### PROCEDURE D-1. MOISTURE BY CARBON TETRACHLORIDE DISTILLATION

The distillation method is suitable for regular dynamites, but the Karl Fischer Method, D-1a, should be used for dynamites that contain aluminum, or for those that are high in  $\text{NH}_4\text{NO}_3$  and low in NG.

For the distillation method follow the procedure given under "General Methods," p. 1289. The amount of sample taken for the determination depends upon the expected water content, and upon whether the 6.0-ml. or 1.0-ml. receiving tube is used. With the 6.0-ml. tube, refluxing is usually conducted for 1 hr., and



with the 10 ml tube the refluxing time is 30 min to 1 hr depending on the type of sample tested

Always dispose of the  $\text{CCl}_4$  extract by pouring it into an appropriate waste receptacle containing absorbent material

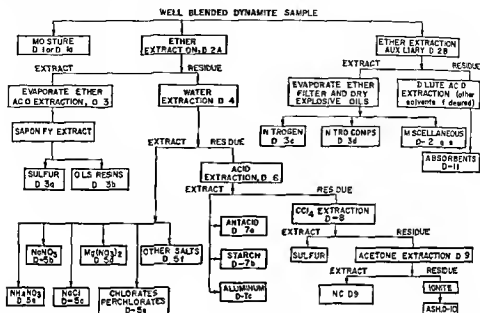


FIG 32 11 Dynamite Analysis Flow Sheet (Courtesy Hercules Powder Co Wilmington Delaware)

### PROCEDURE D 1a MOISTURE BY THE KARL FISCHER TITRATION

Use the procedure described for Karl Fischer Titration under General Methods (p 1290) with the following specific directions

**Procedure**—Accurately weigh 10 g of sample into a dry 250 ml volumetric flask. Make up to the mark with absolute methanol mix and allow to stand until the supernatant liquid is clear; this usually requires about 1 hr. Transfer a 25 ml aliquot to a dry titration flask; quickly close the flask and immediately titrate with Karl Fischer reagent. Run a blank on 25 ml of the methanol used.

### PROCEDURE D 2 ETHER EXTRACTION

**Caution**—Diethyl ether ACS grade anhydrous is used for the extraction of dynamites. It must be free from peroxides. If peroxides are present an explosion may occur during the extraction or in the subsequent evaporation of the ether extract. The following test is recommended by the Institute of Makers of Explosives: add 1 ml of a solution of 5% cadmium iodide, 5% potassium iodide and 90% water to 10 ml of ether in a glass stoppered bottle; shake several times during a period of 1 hr; keeping the bottle in the dark; orange color in the solution indicates peroxide.

**Procedure A**—Place 40 ml of ether in the tube (47 mm I.D. by 275 mm length) of a Wiley extractor (Fisher Scientific Co. No 9605 or equivalent). Weigh exactly 10.000 g of blended sample into a tared Gooch crucible carrying an asbestos

mat, assemble the apparatus and adjust the temperature of the water bath so that ether falls into the crucible in a steady stream and filters through the crucible without overflowing it. (A glass filter paper may be used in place of asbestos, provided an ash determination is not later required.) Time for complete extraction varies from 2 to 4 hr. or longer, depending on the type of dynamite.

Remove the crucible from the extractor, dry it by suction until all odor of ether is gone, and then dry in an oven (safety type steam or electric) for 2 to 3 hr. at 95°C. or overnight at 70°C. Cool in a desiccator and reweigh.

$$\text{Ether soluble, per cent} = \frac{\text{loss in weight} \times 100}{\text{sample weight}} - \text{percentage of moisture}$$

NOTE.—The ether solubles include NG, DNT, TNT, MNT, EGDN, DEGDN, TNDG, paraffin oil, phthalates, coatings (from ammonium nitrate, etc.), the oils and resins naturally occurring in the carbonaceous dopes, and part of any sulfur which may be present.

*Procedure B (Auxiliary Extract).*—The amount of explosive oils derived in the quantitative procedure for percentage of ether solubles described above is usually not adequate for all tests that are desired on the explosive oils. Hence, an additional quantity of about 10 g. is prepared by treating a suitable sample as follows: place a piece of rapid filter paper in a 3-inch Büchner funnel; then fill the funnel from one-quarter to three-quarters full of the dynamite sample; the amount will depend on the explosive oil content of the dynamite, and may be calculated from the value for percentage of ether solubles; pour on 50 ml. of ether, let stand, and then apply suction; repeat with 3 additional 50-ml. portions of ether; transfer the ether-extraction filtrate to a suitable beaker, and evaporate the ether under the combined effect of heat (about 50 to 60°C.) and a dry stream of air; care must be taken to regulate the air jet so as not to cause condensation of atmospheric moisture. The evaporation should be continued until the odor of ether cannot be detected and then 15 min. longer; allow the residue to stand overnight; filter off the oils, resins, and sulfur in the explosive oil, using a small, fast filter paper; store the explosive oil in a calcium chloride desiccator plainly labeled as to its contents.

### PROCEDURE D-3. TREATMENT OF ETHER EXTRACTS

*Sulfur.*—Evaporate the ether extract in a 250-ml. beaker, using a gentle air jet and moderate heat (50–60°C.). After complete removal of the ether, add 50 ml. of 1.0 N alcoholic KOH solution, and cover with a watch glass. Let stand overnight at room temperature, or heat on the steam bath for 4 hr. to saponify the NG and convert the sulfur to a water-soluble form. Remove the watch glass and evaporate to one-half volume, to remove the alcohol.

Transfer quantitatively to a 500-ml. separatory funnel, using about 200 ml. of water. Extract with three 50-ml. portions of ether, and combine the extracts. Save the ether extract for the determination of oils and resins.

To the aqueous layer add 2 ml. of a 1:1 bromine- $\text{CCl}_4$  mixture, 10 ml. of 1:1 HCl, and heat on the steam bath until the bromine is volatilized. Add 10 ml. of 10%  $\text{BaCl}_2$  solution, with stirring. Digest on the steam bath for 1 hr., and filter through a tared Gooch crucible with asbestos mat. Wash free of chlorides with hot distilled water. Dry at 100°C. and heat at 700 to 800°C. for 1 hr. Cool in a desiccator and weigh.  $\text{BaSO}_4 \times 0.13734 = \text{S}$ .

This value is for ether soluble sulfur only for total sulfur determination see Procedure D 8 below

**Oils and Resins**—Evaporate the ether extract retained from the sulfur determination (see paragraph above) to dryness on the steam bath heat the residue for 1 hr at 85°C cool and weigh Calculate weight of residue to percentage of oils and resins

**Nitrogen**—Transfer an accurately weighed sample of  $0.700 \pm 0.050$  g of filtered and dried explosive oil (from an ether extraction of the dynamite) to the decomposition bulb of a du Pont nitrometer with the aid of 5 ml of glacial acetic acid Add 25 ml of 95.0%  $H_2SO_4$  and complete the determination as described in Vol I p 755

Alternatively determine the nitrogen content by the ferrous titanous titration procedure described under Nitroglycerin (Glycerol Trinitrate) by Ferrous Titanous Titration p 1391

**Nitro Compounds** The treatment of the residue obtained by evaporation of the ether from the ether extract depends somewhat on its composition If the residue is essentially solid indicating absence of nitroglycerin omit the treatment with methyl sulfuric acid as described below If sulfur is absent omit the filtration If both nitroglycerin and sulfur are present proceed as follows

Transfer 1.000 g of the filtered dried explosive oil (from an ether extraction) to a 100 ml beaker Add 10 ml of freshly prepared methylsulfuric acid (equal volumes of methanol and 95% sulfuric acid) Heat the beaker on a steam bath for 30 min to destroy the nitroglycerin

Cool add 40 ml of distilled water and transfer the solution to a 250-ml separatory funnel Extract with 50 ml of diethyl ether and draw the water layer off into a second separatory funnel Repeat the extraction with two 25 ml portions of ether and then combine the 3 extracts Wash the combined ether extract first with 25 ml of saturated aqueous  $NaHCO_3$  solution and then with 25 ml of distilled water Discard the wash solutions

Transfer the ether solution to a 150 ml beaker evaporate to dryness on a steam bath and weigh

Nitro compounds per cent

$$= \frac{\text{grams nitro compound} \times \text{percentage of ether soluble (D 2A)}}{\text{grams of explosive oil weighed}}$$

### COLORIMETRIC TESTS FOR NITRO COMPOUNDS

**NaOH/HCl Solutions**—Transfer about 0.1 g of the nitro compounds to a test tube add 10 ml of acetone and stir to dissolve Add 5 ml of 5% aqueous NaOH solution mix and allow to stand for 3 to 5 min Observe the color

Acidify the solution with 1:1 HCl and again observe the color after 3 to 5 min  
**( $NH_4$ )<sub>2</sub>S Solution**—Transfer another 0.1 g portion of the nitro compounds to a test tube add 10 ml of acetone and stir to dissolve Add 5 ml of methanol 5 ml of filtered ammonium sulfide solution mix and allow to stand for 3 to 5 min Observe the color

Refer to Table 32.5 and on the basis of the colors formed report which nitro compound is present

It is advisable to make simultaneously colorimetric tests on known samples of

TABLE 32-5. COLOR REACTIONS OF DINITROTOLUENE (DNT) AND TRINITROTOLUENE (TNT)

Test Solutions	Color Formed	
	DNT	TNT
Acetone-NaOH	blue	red
Acetone-NaOH-HCl	greenish yellow	red
Acetone-methanolic (NH <sub>4</sub> ) <sub>2</sub> S	no coloration	red

DNT and TNT, and compare the exact colors formed. If the color formed by the unknown is not clear-cut, add either DNT or TNT to a fresh portion of the sample, and repeat the tests. The explosive oils may also be analyzed for nitrate nitrogen and nitro nitrogen by the ferrous-titanous procedure described under "Dinitrotoluene by Titanous Chloride Reduction," in "Method When Nitrate Esters Are Present in the Propellant," p. 1384, and in "Nitroglycerin (Glyceryl Trinitrate) by Ferrous-Titanous Titration," p. 1391. If nitro nitrogen is found, apply the above described procedure for destruction of NG and identification of DNT and TNT in the explosive oils, and calculate the quantity of nitrocompound present.

#### PROCEDURE D-4. WATER EXTRACTION

*Procedure.*—Extract the crucible and residue from the ether-soluble determination with about 200 ml. of distilled water added in 6 or 7 portions. Retain the extract for the determination of salts.

Dry the water-extracted residue for 4 hr. or overnight at 95°C., cool in a desiccator, and weigh. Calculate loss in weight to percentage of water soluble.

Samples that contain flour or similar materials are difficult or practically impossible to extract with water, and are treated as follows: transfer the entire ether-insoluble residue to a 250-ml. volumetric flask with water, dilute to the mark, mix, and let settle; use aliquot portions of the clear supernatant liquid to determine the salts present (NH<sub>4</sub>NO<sub>3</sub>, NaNO<sub>3</sub>, NaCl, etc.).

#### PROCEDURE D-5. TREATMENT OF WATER EXTRACT— DETERMINATION OF SALTS

*Procedure.*—Transfer quantitatively the filtrate from the water extraction to a 250-ml. volumetric flask, dilute to the mark, and mix thoroughly. If foam rises in the neck, it may usually be dispelled by adding a drop of ether. Transfer the solution to a clean dry bottle, and stopper until ready to take aliquot portions for analysis.

The water soluble ingredients that may be present are ammonium nitrate, sodium nitrate, and sodium chloride, along with the water-soluble portion of the carbonaceous dope, and traces of calcium and zinc salts. The total salts present

in solution, when determined by the following methods, should equal the loss in weight due to water extraction, or show an "unidentified" value of not more than 1.0%

**Ammonium Nitrate.**—Using an aliquot of the water extract, determine ammonium nitrate by the formaldehyde method as described under "Assay by Formaldehyde Method," p 1313

**Sodium Nitrate.**—Pipet 50 ml of the water extract into a tared 80 or 90 mm porcelain evaporating dish, add 5 ml of 40%  $\text{H}_2\text{SO}_4$ , and evaporate to near dryness on a steam bath. Continue the evaporation over a low flame or an electric hot plate until all the ammonium salts are volatilized and the excess  $\text{H}_2\text{SO}_4$  is driven off. This must not be done too rapidly, otherwise sodium salts may be lost by spattering. When no more fumes of  $\text{SO}_3$  are visible, heat at  $900^\circ\text{C}$  to constant weight, preferably in a muffle. Cool and weigh the resulting  $\text{Na}_2\text{SO}_4$ .  $\text{Na}_2\text{SO}_4 \times 1.197 = \text{NaNO}_3$ . If the amount of  $\text{NaCl}$  is 1.0% or higher apply a correction as follows:

Corrected percentage of  $\text{NaNO}_3$

$$= \text{percentage of } \text{NaNO}_3 \text{ uncorrected} - (1.45 \times \text{percentage of } \text{NaCl})$$

**Chlorides as  $\text{NaCl}$ .**—Pipet 25 ml of the water extract into a 500 ml Erlenmeyer flask. Add 100 ml of distilled water, and determine chlorides by the Volhard procedure as described on p 1312

$$\text{Chlorides as } \text{NaCl}, \text{ per cent} = \frac{5.845(\text{AN} - \text{BN})}{W} \quad (\text{See Eq. 32-4})$$

**Magnesium Nitrate.**—Magnesium nitrate is rarely used. If it is present determine magnesium by the conventional gravimetric method, weighing  $\text{Mg}_2\text{P}_2\text{O}_7$  as the final product

$$\text{Mg}_2\text{P}_2\text{O}_7 \times 2.304 = \text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$$

**Chlorates and Perchlorates.** *Qualitative.*—It is necessary to remove any chloride present, reduce the  $\text{ClO}_3^-$  and  $\text{ClO}_4^-$  to  $\text{Cl}^-$ , then test qualitatively with  $\text{AgNO}_3$  solution

For chlorate, acidify a 25 ml portion of the water extract with a few milliliters of  $\text{HNO}_3$ , then add 5 ml of 10%  $\text{AgNO}_3$  solution. Heat to boiling and digest until the  $\text{AgCl}$  is coagulated, then filter. Disregard the  $\text{AgCl}$ . To the clear filtrate, add 5 ml of 6%  $\text{H}_2\text{SO}_4$  (sulfurous acid) and boil the solution until the odor of  $\text{SO}_2$  can no longer be detected, this usually requires 10 min. Add a few milliliters of  $\text{AgNO}_3$  solution, a white precipitate of  $\text{AgCl}$  shows that  $\text{ClO}_3^-$  was present.

Perchlorate is not reduced by  $\text{H}_2\text{SO}_4$  and, if present, will remain unchanged in the filtrate. Evaporate the filtrate to dryness on the steam bath in a platinum crucible. Add 5 g of  $\text{Na}_2\text{CO}_3$ , mix, and heat over a burner until a clear melt is obtained. After cooling, dissolve in water, acidify with  $\text{HNO}_3$ , and add  $\text{AgNO}_3$  solution. A white precipitate of  $\text{AgCl}$  shows that  $\text{ClO}_4^-$  was present. In order to obtain a valid test for perchlorate, all chlorate must be reduced in the treatment with  $\text{H}_2\text{SO}_4$ .

*Quantitative.*—The chlorate determination is made on a portion of the original water extract and must, therefore, be corrected for any chlorides that are present

Dilute a 25-ml. aliquot of the water extract of the explosive to about 150 ml., and add 10 ml. of 6%  $\text{H}_2\text{SO}_3$ . Boil the solution until the odor of  $\text{SO}_2$  can no longer be detected, usually 10 min. Add 2 ml. of 1:3  $\text{HNO}_3$ , and 50 ml. of approximately 0.1  $N$   $\text{AgNO}_3$  solution. Cover the beaker containing the mixture with a watch glass, and heat on the steam bath for 30 min. Filter off the precipitated silver chloride, wash, dry for 2 hr. at  $110^\circ\text{C}$ ., cool in a desiccator, and weigh.

Calculate the results as sodium or potassium chloride as appropriate.

The perchlorate determination is made on a portion of original water extract, and must, therefore, be corrected for any chlorides plus chlorates that were present.

Evaporate a 25-ml. aliquot of the water extract to dryness in a platinum crucible. Add 5 g. of anhydrous  $\text{Na}_2\text{CO}_3$  to the crucible, and mix. Heat carefully, then ignite until a clear melt is obtained, and continue heating for a period of 15 to 20 min. Cool the melt, dissolve in dilute  $\text{HNO}_3$ , and determine the chloride by precipitation with  $\text{AgNO}_3$ .

If both chloride and chlorate are present, in addition to perchlorate, this determination gives the sum of all 3 of these ingredients weighed as silver chloride.

The result is corrected for the chloride and chlorate present and calculated to the sodium or potassium salt as follows:

$$\text{Weight AgCl} \times 0.4078 = \text{weight of NaCl},$$

or

$$\text{Weight AgCl} \times 0.5205 = \text{weight of KCl}.$$

$$[\text{Weight NaCl} - (a + c)] \times 2.095 = \text{weight NaClO}_4$$

$$[\text{Weight KCl} - (b + d)] \times 1.858 = \text{weight KClO}_4$$

where  $a$  = weight NaCl originally present as such in aliquot taken,

$b$  = weight KCl originally present as such in aliquot taken,

$c$  = weight of NaCl equivalent to the  $\text{NaClO}_3$  originally present in the aliquot taken, and

$d$  = weight of KCl equivalent to the  $\text{KClO}_3$  originally present in the aliquot taken.

These results are then calculated to percentages.

**Other Salts.**—Salts, other than those covered by analytical procedures already presented, are not frequently used in dynamites. Zinc salts or calcium nitrate may sometimes be found in nitrostarch explosives. Sugar has occasionally been added to dynamites.

Zinc can usually be precipitated as the carbonate and ignited to the oxide,  $\text{ZnO}$ .

Calcium is determined by the conventional precipitation as oxalate and measured by the  $\text{KMnO}_4$  titration.

Sugar may be estimated by means of the polarimeter or by the Fehling solution method.

Potassium may be determined by the tetraphenylboron procedure (p. 1400) or by flame photometer (p. 1376).

#### PROCEDURE D-6. ACID EXTRACTION

The purpose of the acid extraction is to remove the antacid in the sample, and thereby permit its subsequent estimation, i.e., calcium carbonate and infrequently zinc oxide (in the presence of ammonium salt, a portion of zinc oxide present will appear in the water extract).

Two procedures are given (a) acid extraction at room temperature, in the absence of starch and (b) acid extraction on boiling in the presence of starch

The presence of metallic aluminum which is encountered in some powders, will interfere. If the determination of metallic aluminum is desired, see Procedure D 7, Aluminum Metallic (Acid Extraction) below

Test for starch by placing a portion of the residue in a small beaker, add 10 ml of water, and bring to a boil. Cool and add a drop of iodine solution. A blue color indicates starch.

**Acid Extraction (Absence of Starch)**—In the absence of starch, extract the dried residue from the water extraction determination with 100 to 150 ml of dilute (1:10) HCl at room temperature. Add the acid in small increments allowing sufficient retention in the Gooch crucible for reaction to take place. Usually 6 increments are sufficient. Wash the residue thoroughly with water to remove all excess acid, and then dry in an oven at 100°C for 4 hr or overnight at 85°C. Cool in a desiccator and reweigh. Retain this Gooch crucible for further treatment. Save the filtrate for the determination of antacid (calcium or zinc). Calculate the loss in weight to percentage of acid soluble (antacid).

**Acid Extraction (Presence of Starch)**—In the presence of starch transfer the dried residue from the water extraction determination quantitatively to a 400 ml beaker with the aid of 180 ml of water. Add 25 ml of 1:10 HCl and digest just below the boiling point for 2½–3 hr on a water bath. This step may be accomplished by suspending the beaker with the aid of a suitable sized concentric ring from a steam bath in an 800 ml beaker filled with hot water and maintained at the correct temperature on a hot plate. The water levels in both beakers should be maintained at their original levels during the entire heating period.

Filter through the original Gooch crucible and dry the extracted residue at 100°C for 4 hr or overnight at 85°C, cool and weigh. The total loss in weight represents the total starch and the antacid. Retain the Gooch crucible and its contents for further treatment.

#### PROCEDURE D 7 TREATMENT OF ACID EXTRACT

**Antacid.** Calcium as  $\text{CaCO}_3$ —Determine calcium in the acid washings remaining from D 6 by precipitation as the oxalate and titration with standard  $\text{KMnO}_4$  solution.

**Zinc as  $\text{ZnO}$** —If zinc is present, use a 50 ml aliquot of the acid extract combined with a 50 ml aliquot of the water extract. Evaporate to dryness on a steam bath, and then heat the beaker on a hot plate (or expel  $\text{NH}_4\text{NO}_3$ ) until disappearance of white fumes. Take up this residue in 2 ml of HCl followed by 100 ml of distilled water, neutralize with  $\text{NH}_4\text{OH}$ , and precipitate zinc as the sulfide with  $\text{H}_2\text{S}$ . Filter out the precipitate, dissolve it in dilute HCl, and boil the solution to expel  $\text{H}_2\text{S}$ . Complete the determination of zinc by the EDTA titration as described under Zinc Oxide Assay, p 1343.

**Starch**—Subtract the weight of Antacid, Procedure D 7, Antacid, from the loss in weight of the sample on acid extraction, Procedure D 6 and calculate the difference to percentage of starch.

**Aluminum, Metallic (Acid Extraction)**—Use the Gooch crucible containing the dried residue from the water extraction Procedure D 4.

Transfer the residue from the crucible to a 400 ml beaker, and add 100 ml of distilled water. Then add concentrated HCl, using 5 ml of the acid for samples

containing up to 2% of aluminum and no antacid, and using 10 ml. of the acid for samples containing up to 3.5% aluminum and 0.5%  $\text{CaCO}_3$ . For samples exceeding either of these conditions, add more  $\text{HCl}$  proportionately. Stir the solution, breaking up all lumps, cover with a watch glass, and heat almost to the boiling point on a steam bath. Continue heating with occasional stirring until all of the aluminum is dissolved. Usually about 30 min. are required.

After heating, remove the beaker and filter while hot through the same Gooch crucible. Wash the beaker and crucible with distilled water.

Dry the crucible and residue in a  $100^\circ\text{C}$ . oven for 4 hr., cool, and weigh. For samples containing no antacid, calculate loss in weight to percentage of aluminum. For samples containing both aluminum and  $\text{CaCO}_3$ , calculate loss in weight to percentage of total acid extract. Then determine the amount of calcium in the filtrate in terms of  $\text{CaCO}_3$  by Procedure D-7, Antacid.

Metallic aluminum, per cent = percentage of total acid extract — percentage of  $\text{CaCO}_3$ .

Alternatively, aluminum may be determined by the EDTA titration, as described by Welcher.<sup>24</sup>

#### *PROCEDURE D-8. CARBON TETRACHLORIDE EXTRACTION (FOR SULFUR)*

In case the sample does not contain sulfur, omit this extraction and apply Procedure D-9.

**Procedure.**—Place the Gooch crucible, containing the residue from the acid extraction, in a 50-ml. beaker, and add enough  $\text{CCl}_4$  to fill the crucible and the beaker to within about  $\frac{1}{8}$  in. of the top. Heat this assembly on a steam bath until the solvent in the beaker outside the Gooch crucible has been evaporated to a volume of about 5 ml. Remove from the steam bath and filter the remaining  $\text{CCl}_4$  in the crucible into a filter flask. Add more  $\text{CCl}_4$  to the crucible and repeat the evaporation procedure, filter, and wash the crucible with hot  $\text{CCl}_4$ . Test for completeness of extraction by evaporating a portion of the fresh filtrate on a watch glass, and noting whether any residue is obtained. At the end of the extraction period, transfer the Gooch crucible and contents to an oven at  $100^\circ\text{C}$ . for 2 hr., cool, and reweigh. Calculate loss in weight to percentage of sulfur.

The sum of the sulfur found here and by Procedure D-3, Sulfur represents the total sulfur content.

**NOTE.**—Some analysts prefer to determine total sulfur by extraction with a 1:1 mixture of diethyl ether and carbon bisulfide. They also favor this mixed solvent in the general scheme of analysis, and consequently follow a system that would be represented by a flow sheet differing significantly from that of Fig. 32-11.

Save the crucible and residue for the nitrocellulose determination.

#### *PROCEDURE D-9. ACETONE EXTRACTION (FOR NC)*

**Procedure.**—Transfer the residue from the acid extraction (absence of sulfur), or the residue from the  $\text{CCl}_4$  extraction (if sulfur was present), to a tall 400-ml. beaker. Add 50 ml. of acetone to the beaker, and heat to boiling on a steam bath. Continue to boil until all nitrocotton is in solution, as evidenced by the disappearance of all lumps and free dispersion of all insoluble material. Remove

<sup>24</sup> Welcher, F. J., *The Analytical Uses of Ethylenediaminetetraacetic Acid*, D. Van Nostrand Co., Inc., Princeton, 1958.



from the steam bath and add enough acetone to fill the beaker to within about  $\frac{1}{2}$  in. of the top. Cover with a watch glass and let stand until all solids have settled to the bottom (usually overnight settling time is required). Decant or siphon the clear supernatant liquor containing the soluble nitrocotton and discard. Filter the remainder through the original Gooch crucible. Wash the contents of the crucible with acetone until all the soluble material has been removed as evidenced by the absence of precipitate when the filtrate is mixed with water. Dry in an oven for 2 hr. at  $100^{\circ}\text{C}$ . cool and reweigh. Calculate loss in weight by acetone extraction to percentage of nitrocotton. Retain the Gooch crucible and its contents.

#### PROCEDURE D 10 ASH IN ABSORBENTS

After the acetone extraction heat the crucible over a flame in a hood until most of the organic material has been removed. Then place it in a muffle furnace until combustion is complete, cool and reweigh.

If an ash content above 1.5% on the original powder basis is obtained a microscopic examination should be made. Materials usually found in this residue are kieselguhr, fuller's earth, bentonite, ferrosilicon and materials of a related character, also iron oxide and any metals insoluble in HCl may be present. When the dynamite contains coal the ash will be relatively high and is likely to be red because of the presence of  $\text{Fe}_2\text{O}_3$ .

#### PROCEDURE D 11 EXAMINATION OF ABSORBENTS

If the ash determination is not required the residue from the acetone extraction may be used for a qualitative examination for type of absorbents. If the residue from the acetone extraction was ashed, extract 5 to 10 g. of the original sample for 2 hr. with diethyl ether in a Wiley or Soxhlet apparatus. Air-dry the residue until no odor of ether is perceptible.

Transfer the residue to a 4 in. watch glass. Pick it apart with a dissecting needle and examine it with a powerful hand lens or a low power microscope to identify the various materials.

A set of samples of absorbents commonly used in dynamite is indispensable for comparison with unknown samples. Even with a good set of known specimens the sure identification of unknowns is likely to prove difficult. The task is one in which previous training and extensive experience are of great value.

#### PROCEDURE D 12 EXTENDED EXAMINATION OF EXPLOSIVE OILS

In addition to the determination of the more common ingredients described under Procedure D 3, it may be desirable to examine the explosive oils for a variety of less commonly used ingredients. Brief outlines for a few ingredients or combinations of ingredients are as follows:

**Identification of Sucrose Octantrate (SOT).—**Dissolve a small portion of the explosive oil in methanol and add a little ammonium sulfide (or zinc dust + dilute HCl). After the reaction is complete and solids have settled, decant the supernatant liquid and test with Fehling's reagent. A bright red precipitate of cuprous oxide indicates reducing sugar.

The optical rotation of nitrosugar may also be used for identification. The amount present may be determined quantitatively using the polarimeter.

measurements the final results are calculated by the method of successive approximations. For example the first approximation for NG will be as follows:

$$\text{NG per cent} = \frac{(A_t - A_c - A_s)100}{a}$$

where  $A_t$  = total absorbance at  $9.2 \mu$  of cell filled with benzene solution of the sample

$A_c$  = absorbance of cell at  $9.2 \mu$ ,

$A_s$  = absorbance of benzene at  $9.2 \mu$  (i.e., absorptivity of benzene at  $9.2 \mu$  multiplied by its weight fraction. For a 20% solution of sample benzene is 80% and its weight fraction is 0.80), and

$a$  = average absorptivity of NG at  $9.2 \mu$  as determined in the preliminary (standardization) measurements

Then if the value obtained was for a 20% solution of sample the value for the original sample will be 5 times the value found.

A second approximation is then made for NG taking into account a corrective value for the absorbance of EGDN at  $9.2 \mu$  which is obtained by using the first approximation of the NG content to calculate the ratio of NG and EGDN in the solution and then applying the absorptivity value for EGDN as determined in the preliminary (standardization) measurements.

Successive approximations are then carried out for both NG and EGDN until the values become practically constant.<sup>26</sup>

#### ANALYSIS OF WRAPPER

**Procedure**—Weigh 1 whole wrapper and fold it so that it may be inserted in a Soxhlet extractor below the level of the siphon tube and extract with diethyl ether. Determine paraffin, nitroglycerin, paper, ash, and moisture.

If nitroglycerin has leaked from the powder and is present in the wrapper it will be seen under the extracted paraffin after evaporation of the ether. After weighing the total ether extractive matter determine nitroglycerin by the ferrous-titanous titration (p. 1391). Total extractive matter minus nitroglycerin is considered to be paraffin.

Remove the extracted paper from the Soxhlet apparatus, place it on a watch glass, and let it stand in a warm atmosphere until all odor of ether is gone. Place the paper in an aluminum can and dry in an oven at  $100^\circ \pm 5^\circ\text{C}$  for 1 hr., cool in a desiccator, place a cover on the can, and weigh. This weight (minus the tare of can and cover) is considered to represent dry paper and ash. Incinerate the dry paper in a tared platinum dish until all carbonaceous matter is volatilized, cool in a desiccator, and reweigh. The residue represents ash. Calculate moisture as the difference 100% minus dry paper, ash, paraffin, and NG (all on per cent wet basis). If desired a separate moisture determination may be made by heating a weighed, rolled strip of the original paper in an oven for 3 hr. at  $95^\circ\text{C}$ .

When the amount of nitroglycerin is appreciable and if the purpose of the analysis is to determine the composition of the dynamite as originally manufactured, the composition of the wrapper should be calculated to a nitroglycerin-free basis and the analysis of the dynamite recalculated to include the nitroglycerin found in the wrapper.

<sup>26</sup> A more detailed presentation of the iterative procedure (method of successive approximations) as applied to analysis by infrared is given by Fistera, *J. in Applied Spectroscopy*, 7, 115, 1953.

## BLASTING CAPS AND ELECTRIC DETONATORS

The commercial blasting caps and electric detonators loaded with a mixture of mercury fulminate and potassium chlorate, which were in general use in the United States some years ago, have now been largely displaced by compound detonators, in which a priming charge of mercury fulminate, lead azide, lead styphnate, lead mononitrate resorcinate, diazodinitrophenol, hexanitromannite, or other primary explosive is employed to initiate a main charge of tetryl, TNT, PETN, picric acid, or other nitrocompound.

## PREPARATION OF SAMPLE

In the examination of blasting caps or detonators for either commercial or military use, the removal of the detonating composition from the copper, aluminum, or brass shell requires considerable precaution. Blasting caps are emptied by squeezing the cap gently in a pair of "gas forceps," the jaws of the forceps being passed through a small opening in a piece of heavy leather, rubber belting, or similar material, about 6 in. square, which serves as a shield to protect the hand in case of explosion of the cap in squeezing. After each squeeze, the loosened portion of the charge is shaken out on a piece of glazed paper, the cap is turned slightly in the forceps, and again squeezed. The pressure on the cap should be just sufficient to dent it slightly and, in shaking out the charge, the cap should not be tapped on the table or other surface. Another method of removing the charge is by rolling the cap between 2 pieces of hardwood board, and emptying the loosened portion of the charge after each rolling.

Electric detonators<sup>27</sup> are opened by first cutting off the wires or "legs" close to the shell, then tearing off the upper portion of the shell by means of pointed side-cutting pliers, the cap being held firmly in the fingers, and a thin strip of the copper shell being torn off spirally by nipping the top edge of the shell with the forceps. This must be done with great care, especially when the portion of the shell containing the fulminate charge is approached. When the greater portion of the plug that holds the wires in place has been exposed, the plug and wires are gently pulled out, care being taken to avoid undue force and possible friction. Any adhering particles of the charge are brushed off onto glazed paper. The charge is then removed from the lower part of the shell just as in the case of blasting caps.

The charge is removed separately from several of the caps or detonators, and each is weighed in order to determine the average weight of charge as well as variation of the charge weights.

Reinforced caps, or those which contain a small, perforated, inner copper capsule pressed on top of the charge, must be opened in the manner described for electric detonators, in order to remove the inner capsule. Detonators of this type usually contain a main charge of some nitrocompound superimposed by a layer of mercury fulminate, a mixture of fulminate and chlorate, or lead azide. Although a clean mechanical separation of the 2 layers is usually not possible, portions can be taken from each and identified by qualitative tests, before proceeding with a quantitative examination.

<sup>27</sup> A safe apparatus for cutting open electric detonators is shown in Taylor, C. A., and Rinkenbach, W. R., Bureau of Mines Technical Paper, No. 282, Analysis of Detonating and Priming Mixtures, Plate I, 1922.

precipitate that may be filtered off, washed with water and then with alcohol, dried in the air, and tested by striking a small portion with a hammer.

## PRIMERS

### VARIATIONS IN COMPOSITION

Many varieties of composition are used in primers for small arms ammunition, and for other military purposes. The composition must be ignited by the impact of the firing pin, and must give a flame of sufficient intensity and duration to ensure proper ignition of the propellant or of the detonator, depending on the purpose for which the primer is employed. As primers are used with various kinds and granulation of explosives, a priming composition suitable for one purpose is unsuited for another.

Table 32-6 gives a few examples of the great variety of patented types of the

TABLE 32-6. MODERN NONCORROSIVE TYPES OF PRIMER COMPOSITIONS

Ingredients	Compositions, per cent						
Mercury fulminate	—	30-35	25-40	—	30-31.5	37	35-40
Lead styphnate	38	—	5-10	—	10-5.5	—	—
Barium nitrate	39	—	24-44	—	29-30.5	32	0-16
Lead nitrate	—	—	—	30	—	—	30-12
Lead peroxide	5	—	—	—	—	—	—
Barium peroxide	—	25-45	—	—	—	—	—
Calcium silicide	11	10-25	—	—	—	—	—
Antimony sulfide	5	—	0-16	—	—	28	—
Lead thiocyanate	—	—	—	7	10-10.5	—	12-10
Diazodinitrophenol	—	—	—	6-8	—	—	—
Tetracene	2	—	—	—	—	—	—
Basic lead picrate	—	—	—	38-36	—	—	—
Lead dinitrosalicylate	—	—	4-10	18	—	—	—
Abrasive	—	0-25	0-30	—	20-21	3	22-21

more modern noncorrosive primer compositions in which potassium chlorate has been eliminated because the chloride formed as one of the products of combustion was found to be responsible for the corrosion of gun barrels. Two mixtures containing potassium chlorate that are still very commonly used, but are not shown in Table 32-6 are:

(1) A primer mixture for detonators;

Potassium chlorate	33.4% by weight
Antimony sulfide	33.3% by weight
Lead azide	28.3% by weight
Carborundum	5.0% by weight

and

## (2) An ignition mixture for electric primers

Potassium chlorate	60% by weight
Diazodinitrophenol	20% by weight
Nitrostarch	5% by weight
Charcoal	15% by weight

In addition to the ingredients shown in Table 32.6, most priming compositions are mixed with small amounts of some binding material dissolved in water or alcohol, such as gum arabic, gum tragacanth, glue, shellac, etc. These traces of binding materials are usually disregarded in the analysis of the compositions.

## PREPARATION OF SAMPLE

If the caps contain anvils these as well as any covering of tin foil or paper must first be carefully removed. The primer composition is then carefully removed from a number of primers and weighed to determine the average charge. It is then crushed a little at a time, and the sample is well mixed. If necessary, the primer may be removed from the caps by the aid of water or alcohol and the transfer liquid removed by evaporation before weighing.

## QUALITATIVE EXAMINATION

The following special tests may be used in connection with a qualitative analysis of the mixture.

A small amount is burned between 2 watch glasses the formation of a mirror indicating mercury antimony copper or lead. The mercury mirror is readily volatile on gentle ignition.

A portion of the mixture is successively extracted with diethyl ether, water  $\text{Na}_2\text{S}_2\text{O}_3$  solution and aqua regia, each of the solutions being retained for examination.

TNT or tetryl may be present in the ether solution and are identified by a melting point test. Sulfur is detected by burning a portion of the ether soluble material and observing for the odor of  $\text{SO}_2$ .

The water extract is tested for  $\text{KClO}_3$  by adding  $\text{H}_2\text{SO}_4$  boiling and observing for the odor of chlorine. A portion is treated with  $\text{HCl}$  and  $\text{FeCl}_3$  a red color indicating thiocyanate. The  $\text{FeSO}_4$  ring test is made for nitrates. A white precipitate with  $\text{H}_2\text{SO}_4$  indicates barium or lead.

The aqua regia solution is diluted and tested with  $\text{H}_2\text{S}$  for antimony, lead and copper. If the precipitate is not orange-red, lead or copper is indicated. The precipitate is dissolved in  $\text{HNO}_3$  and neutralized with  $\text{NH}_4\text{OH}$ , a blue solution indicates copper. Lead is detected by the formation of a white precipitate with  $\text{H}_2\text{SO}_4$ .

Any material insoluble in aqua regia may be powdered glass or other abrasive material.

## QUANTITATIVE ANALYSIS

The method of analysis will depend entirely upon the ingredients indicated by qualitative tests. In general, a separation is effected by successive extractions with solvents such as diethyl ether, water  $\text{Na}_2\text{S}_2\text{O}_3$  solution (to remove fulminate) dilute or concentrated  $\text{HCl}$  and aqua regia. The loss in weight of a sample by extraction with a specified solvent is frequently used as the quantitative measure.

of an ingredient. In some cases the materials in the water and acid solutions are determined by conventional gravimetric, titrimetric, or instrumental methods. Some of the specific directions given under "Dynamites" may be adaptable to the quantitative analyses of primer compositions. Two typical examples are as follows:

*EXAMPLE 1: DETONATOR PRIMER COMPOSITION CONTAINING POTASSIUM CHLORATE, ANTIMONY SULFIDE, LEAD AZIDE, AND CARBORUNDUM*

**Moisture.**—Dry a 0.4- to 0.7-g. sample to constant weight at 55° to 65°C. in a desiccator containing  $\text{CaCl}_2$ .

**Potassium Chlorate.**—Weigh a 1.0-g. sample into a tared, ignited, filtering crucible containing an asbestos mat. Add 3 ml. of a saturated aqueous solution of lead azide at  $25^\circ \pm 2^\circ\text{C}$ . Agitate for about 1 min. with a glass rod, breaking up lumps if necessary. Apply suction. Repeat this treatment with aqueous lead azide solution 5 times (total of six 3-ml. extractions). Rinse the crucible with ethanol, then with diethyl ether. Dry by suction, and then at about 95°C. for 15 to 20 min. Cool in a desiccator, and reweigh. Consider the loss in weight to represent  $\text{KClO}_3$ .

**Lead Azide.**—Extract the residue from the potassium chlorate determination with successive 5-ml. portions of saturated ammonium acetate solution at about 25°C. until the washings test free from lead, on addition of a few drops of potassium dichromate solution. Avoid excessive washing with the acetate solution; not more than 60 ml. should be required. Rinse the crucible with distilled water, ethanol, and diethyl ether in succession. Dry by suction, then at about 100°C., cool in a desiccator, and reweigh. Consider the loss in weight to represent  $\text{Pb}(\text{N}_3)_2$ .

**Antimony Sulfide.**—Extract the residue from the lead azide determination with cool, concentrated HCl until most of the antimony sulfide has dissolved. Then rinse the crucible thoroughly with hot concentrated HCl. Ignite the crucible to remove sulfur liberated by the acid treatment, then cool in a desiccator, and reweigh. Consider the loss in weight to represent  $\text{Sb}_2\text{S}_3$ .

**Carborundum.**—Consider the residue in the crucible after the antimony sulfide determination to be carborundum.

*EXAMPLE 2: PRIMER COMPOSITION CONTAINING BARIUM NITRATE, NORMAL OR BASIC LEAD STYPHNATE, TETRACENE, ANTIMONY SULFIDE, AND LEAD AZIDE*

**Moisture.**—Same as for Example 1.

**Barium Nitrate.**—Extract the  $\text{Ba}(\text{NO}_3)_2$  from a 0.5-g. sample in a tared, medium-porosity, fritted-glass crucible by repetitive additions of distilled water saturated with lead azide and application of suction. Rinse with ethanol, aspirate, dry at 55° to 65°C. for 30 min., cool, and reweigh. Consider the loss in weight to represent  $\text{Ba}(\text{NO}_3)_2$  and moisture.

**Normal or Basic Lead Styphnate.**—Extract the residue from the  $\text{Ba}(\text{NO}_3)_2$  determination with successive portions of saturated ammonium acetate solution (25°C.) until the washings are colorless. Then wash the residue with water saturated with antimony sulfide until the washings come through clear. Reserve the crucible for the tetracene determination. Make up the filtrate and washings to a volume of 250 ml. in a volumetric flask by adding sufficient distilled water. Pipet a 2-ml. aliquot to a 100-ml. or 50-ml. volumetric flask (100 for normal or 50 for basic lead styphnate), and dilute to the mark with distilled water. Measure the

transmittance of this solution at 410  $m\mu$  in a 1 cm Corex cell, using a matched cell containing the same concentration of ammonium acetate in the reference beam. Calculate basic or normal lead styphnate from a standard curve determined on known concentrations of the appropriate styphnate.

**Tetracene.**—Wash the residue from the styphnate determination several times with ethanol, aspirate, dry at 55° to 65°C for 30 min, cool, and reweigh. Using a jet of water, transfer the dried residue to a 125 ml beaker, add 25 ml of water, and boil the liquid for 5 min. Filter through the crucible previously used, wash the residue in the crucible with boiling water, and then with ethanol. Aspirate, dry at 55° to 65°C for 30 min, cool, and reweigh. Consider the loss in weight by hot water extraction to represent tetracene.

**Antimony Sulfide.**—Consider the residue in the crucible after the determination of tetracene to represent antimony sulfide.

**Lead Azide.**—Calculate lead azide as the difference from 100% of the sum of the percentages of barium nitrate, lead styphnate, tetracene, and antimony sulfide (dry basis).

# PROPELLANTS

## LIQUID PROPELLANTS

There are relatively few cases in which liquid propellant ingredients are mixed in major quantities, except at the moment of ignition. Some monopropellant mixtures of 2 or 3 major components have been considered, but very few of these are currently in use, except in small scale experimentation. Examples of these are hydrogen peroxide-methanol, ammonia-ammonium nitrate, nitro with nitrate compounds, and methyl nitrate-methanol. Many mixtures are used, however, where a minor quantity of some ingredient is added to a fuel, oxidizer, or monopropellant in order to improve ignitability, lower the freezing point, or reduce corrosive action on containers.

Procedures for chemical analyses of a few liquid propellant materials are presented under the section on ingredients.

## SOLID PROPELLANTS

Conventionally, solid propellants are divided into 2 fairly distinct groups: nitrocellulose-base, and composite. The term "nitrocellulose-base" is applied to homogeneous mixtures of nitrocellulose with various plasticizers, stabilizers, and ballistic modifiers. If the propellants contain no nitroglycerin, they are called "single base"; when they contain nitroglycerin, they are called "double base"; if they contain nitrocellulose, nitroglycerin, and nitroguanidine they are sometimes called "triple base." Composite propellants are nonhomogeneous mixtures of oxidizers and fuels and, until recently never contained nitrocellulose. Formulations have become overlapping with respect to the terms nitrocellulose-base and composite, and both types have become increasingly complex. For example, powdered metals, metal hydrides, and organometallic materials are now being used in both basic types.

## NITROCELLULOSE-BASE SOLID PROPELLANTS

### PREPARATION OF SAMPLES

*Caution.*—Do not apply the grinding procedure given here to propellants containing chlorates, perchlorates, or other materials that could cause grinding to be a hazardous operation. Most nitrocellulose-base solid propellants currently produced can be safely ground, but it should be kept in mind that some change in formulation may create a new sample-preparation hazard.

*Sheet Propellant.*—Cut sheet propellant into pieces approximately  $\frac{1}{8}$  in. square, using beryllium alloy shears. Sheet propellant may be ground in a Wiley mill only if it is sufficiently brittle. Chilling in an ice bath or with dry ice is sometimes done to render soft samples brittle enough for grinding.

*Small Grains.*—To grind small-grain propellant (each grain weighing 0.2 g. or less) use a Standard Model No. 2 G Wiley mill equipped with an explosion-proof



motor and a 20 mesh screen in place between the grinding chamber and the small receiving vessel. Make sure the mill is grounded (protection against the static charge that is produced by the operation of the machine). Use a shield around the equipment and grind only a few grains at a time. Remove each ground increment to a safe location and check the temperature of the mill. Allow time for the rotor and blades to cool between increments if heating is discernible.

**Large Grain Propellant** Cut large grain propellant (pieces larger than 0.2 g.) into uniform slices about 0.15 to 0.20 mm thick using a powder cutter (a modified paper cutter preferably with a beryllium alloy blade) as illustrated in Fig. 32.12.

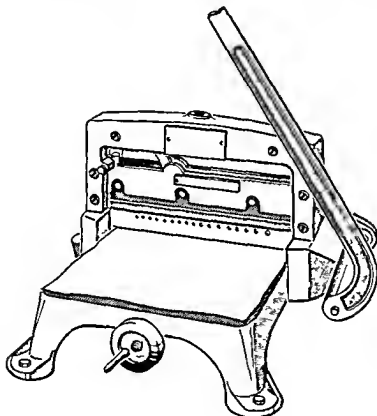


FIG. 32.12 Powder Cutter

Then cut the slices into squares about  $\frac{1}{8}$  in. on the side. Alternatively large grains may be sampled by microtoming slices about 0.02 to 0.03 in. thick provided the material is neither too soft nor too hard.

**NOTE**—Samples prepared by any of the above techniques should be handled so as to expose only small amounts to the atmosphere (or to ignition hazard) at any time. The small increments of a comminuted sample should be placed in a suitable glass bottle immediately as they are prepared and the bottle should be kept stoppered except as necessary to introduce propellant and at a safe distance from the comminuting operation.

#### SOLIFAT EXTRACTION

To achieve partial separation into components, nitrocellulose base propellants are commonly extracted with water-acetic acid (65–70%) diethyl ether, methylon

chloride, chloroform, carbon tetrachloride, methanol, ethanol, or a pentane-methylene chloride azeotrope (2:1 by volume), choice of solvents depending on the formulation and the ingredient(s) to be determined. Other solvents less commonly used are cyclohexane, petroleum ether, morpholine, toluene, benzene, and dioxane. At present, methylene chloride is favored for most extractions with low boiling solvent. Soxhlet or Wiley extraction equipment is most commonly used, but for some purposes tared Selas or Gooch crucibles are used in conjunction with suction devices after refluxing of the sample and solvent in an Erlenmeyer flask.

For safety reasons, water baths or steam baths are used in preference to electric heaters for extractions with low boiling solvents. For higher boiling solvents, electric hot plates or heating mantles are used, but great care is taken to avoid loss of solvent, an event which may lead to violent explosion. Paper thimbles, Alundum thimbles, and filter tubes with sintered glass bottoms are used in the Soxhlet or Wiley extractors.

For safety reasons, as well as technical ones, it is desirable that all the components of a propellant sample be either highly insoluble or highly soluble in the solvent used. For example, a dangerous situation is created if a Soxhlet extraction is made on a sample containing nitroglycerin, using a solvent in which nitroglycerin is only slightly soluble. As time goes on during extraction, the propellant is continuously washed with fresh solvent, which carries some nitroglycerin to the extraction flask where the solvent is being heated. The concentration of nitroglycerin in the flask eventually reaches a point where two phases exist, one of these being undiluted nitroglycerin, which is in contact with heated surfaces.

In making separations by extractive solvents, the time necessary for completion of the extraction is established for each new type of propellant. The test for completion time is frequently made gravimetrically by evaporation in a tared vessel of a portion of freshly produced extract. Sensitive color tests on the fresh extract are useful for certain ingredients, such as nitroglycerin (blue color with 1% diphenylamine in  $\text{H}_2\text{SO}_4$ ). The composition of the propellant, its particle size or thickness of pieces, the siphoning cycle, etc., determine the time required for the complete removal of the ingredients sought. For a given size of sample, extraction is expedited by using the smallest Soxhlet that will hold the material. In contrast with a larger Soxhlet, the smaller one gives a more rapid siphoning cycle and a higher temperature of solvent in contact with the sample.

Nitroguanidine is slightly soluble in methylene chloride (even when water-free) but quite insoluble in carbon tetrachloride or in the pentane-methylene chloride azeotrope mentioned above.<sup>28</sup> Hence  $\text{CCl}_4$  or the azeotrope is advantageous in separating nitroguanidine from ingredients soluble in these solvents.

*Solvent Extractive Matter.*—The amount of solvent extractive matter is usually determined by extracting a weighed sample in a paper thimble in a Soxhlet apparatus, using a prescribed volatile solvent (e.g., methylene chloride) and a tared extraction flask. After an adequate period of operation, the flask is removed from the extraction tube, the volatile solvent is removed by a gentle air stream and very moderate heat, and the flask is reweighed after conditioning in a vacuum desiccator.

<sup>28</sup> Watts, J. D., and Stalcup, Harry, *Anal. Chem.*, **29**, 253, 1957.

## MOISTURE BY DESICCATION

The desiccation method for moisture is applied to solventless double base propellant and to some other specific formulations

**Procedure** Condition and weigh a stoppered weighing dish (60 mm diameter 30 mm depth) Weigh accurately approximately 10 g of propellant into the dish and place it in the desiccator charged with indicating Drierite indicating silica gel or anhydrous calcium chloride Weigh the stoppered dish at 24 hr intervals until the loss in weight between weighings does not exceed 1 mg From the loss in weight calculate the percentage of moisture in the propellant Constant weight is normally attained in 48 to 72 hr

## MOISTURE BY CARBON TETRACHLORIDE DISTILLATION

The carbon tetrachloride procedure for determining water content is applied chiefly to small grain or finely divided cannon and rocket propellants Follow the procedure given in General Methods p 1289 and continue the distillation for the time indicated in Table 327

TABLE 327 DISTILLATION TIMES FOR DETERMINING WATER IN PROPELLANT SAMPLES BY  $\text{CCl}_4$  DISTILLATION

Propellant Web Size in inches	Grain Condition	Distillation Time in Hours
Less than 0.025	Whole	3
0.025 to 0.040	Whole	5
0.040 to 0.060	Whole	10
0.060 to 0.090	Whole	16
	Sliced	6
Over 0.090	Whole	24
	Sliced	8

If desired the condenser and receiving tube may be made water repellent by treatment with a silicone preparation In this case the readings are taken at the point of contact of the top meniscus with the wall of the tube and at the center of the lower meniscus

## MOISTURE AND VOLATILES BY OIL DRYING AT 100°C (See p 1294)

MOISTURE AND VOLATILES BY VACUUM OVEN DRYING AT 55°C  
(See p 1294)

## VOLATILES TOTAL BY SOLUTION EVACUATION PROCEDURE

Certain specifications for cannon and small arms propellants require the determination of total volatiles by the solution evacuation procedure The description of the method is lengthy the procedure requires special apparatus and equipment the operations are tedious and the results are based on a loss in weight found as

a difference between two relatively large weights. The procedure is not reproduced herein but is described in various specifications <sup>8,29</sup> and the open literature.<sup>30</sup> At present, several procedures using less complicated equipment are being investigated with the hope that one of these may serve as a replacement for the solution-evacuation method.

### RESIDUAL SOLVENT

Residual solvent in certain propellants is calculated by subtracting the percentage of moisture (by desiccation or carbon tetrachloride distillation) from the percentage of total volatiles (by the solution-evacuation procedure).

### BARIUM NITRATE OR OTHER BARIUM SALTS

*Procedure.*—A 5-g. sample of propellant is placed in a 90-mm. porcelain evaporating dish, 15 ml. of 70%  $\text{HNO}_3$  are added, and the dish is heated on a steam bath in a hood until reaction starts. The dish is then removed from the steam bath and allowed to stand until the evolution of fumes has ceased. The dish is reheated on the steam bath until dry. It is then placed on a Nichrome triangle and cautiously heated with a flame until all carbonaceous matter is burned off, avoiding overheating, which could cause fusion of the salts with the dish. After cooling, 5 ml. of distilled water and 5 ml. of 38%  $\text{HCl}$  are added, then the dish is covered and heated on the steam bath for 5 to 10 min. The contents of the dish are diluted with distilled water, and filtered through a fine filter paper into a 150-ml. beaker. The dish and filter are thoroughly washed with distilled water. Barium is then precipitated as barium sulfate by the addition of 10 ml. of 5%  $\text{H}_2\text{SO}_4$  to the boiling solution, and the determination is completed by the conventional gravimetric procedure. Potassium salts, if present in the propellant, may be determined on the filtrate from the barium sulfate determination, using the tetraphenylboron procedure or, in simple cases, by gravimetric determination as  $\text{K}_2\text{SO}_4$ .

### CALCIUM SALTS

Calcium in propellants is determined by the morpholine method, EDTA titration, or flame photometer procedure.

*The Morpholine Method.*—The morpholine method is applied chiefly to propellants containing calcium as the carbonate.

*Caution.*—Morpholine fumes are highly flammable and easily ignited by contact with the surface of a hot plate. The heating step in the procedure must be done very carefully.

*Procedure.*—A 5-g. sample is heated in a 250-ml. beaker with 50 ml. of morpholine, using an electric hot plate in a hood. The hot solution is poured through a tared Gooch crucible. The beaker and crucible are washed with an additional 25 ml. of hot morpholine, and then with sufficient cold water to remove the morpholine. The beaker and crucible are washed with several 25-ml. portions of warm distilled water, and then with a small amount of acetone. When most of the acetone has been removed by suction, the crucible is dried in a non-sparking oven at 100°C., cooled in a desiccator, and weighed. The crucible is then washed with not less than 50 ml. of 3 *N*  $\text{HCl}$ , followed by distilled water and acetone. It is

<sup>29</sup> Military specifications, JAN-P-231, JAN-P-309, JAN-P-323, JAN-P-528, JAN-P-668.

<sup>30</sup> Shaefer, W. E., Hall, Robert T., French, John C., and Becker, Walter W., *Anal. Chem.*, 19, 378, 1947.

then dried cooled and reweighed. The loss in weight by the acid treatment is taken as calcium carbonate and calculated to percentage basis.

**The EDTA (Ethylenediammetetraacetic Acid) Method Procedure**—The calcium is extracted from the propellant by refluxing with 70% acetic acid to which about 5% of concentrated HCl has been added. After neutralization with 1 N NaOH and addition of 2 ml excess per 100 ml of solution an aliquot containing not more than 0.05 g Ca is titrated with 0.1 M solution of disodium EDTA using as indicator 5 to 6 drops of a saturated aqueous solution of Murexide. One ml of 0.1 M EDTA = 4.008 mg Ca. (See also footnote 24 given on p. 1361.)

**The Flame Photometer Procedure (Ca, Na, K)**—The flame photometer procedures given below for calcium, sodium, and potassium evolved from an extensive study made by the Joint Army Navy Air Force Panel on Analytical Chemistry of Solid Propellants. They are designed for use with the Beckman DU spectrophotometer equipped with flame attachment and photomultiplier and using acetylene as fuel.

#### General Instrumental Settings for Ca, Na, K

Oxygen pressure from tank	40 psi
Oxygen pressure second stage	10 psi
Acetylene pressure from tank	10 psi
Acetylene pressure second stage	3.5 psi
Selection switch at 0.1	
Photomultiplier zero adjustment—off	
Red sensitive phototube	

**For Potassium (K)** Use 768  $m\mu$  wavelength and a slit width of about 0.08 mm. Set sensitivity 5 turns either way from Full as necessary. Adjust dark current to zero. Aspirate  $KNO_3$  solution of nominal percentage (e.g. 0.5%) Set transmittance at 50% and zero the galvanometer with the slit control. Record and use this slit setting for all K determinations.

**Standards**—Dissolve 8.00 g of potassium nitrate in distilled water and bring to the mark in a 2000 ml volumetric flask. Mix well and transfer to a polyethylene bottle for storage. Dilute a 50 ml aliquot of this solution to 1 liter (corresponding to 0.50%  $KNO_3$  in a 10 g sample). Use dilutions of this standard to establish the standard curve which may not be linear in the higher concentrations. Use the 50 ml to 1 liter dilution to make the 50% transmittance setting prior to the running of samples.

**Sample**—Heat a 10 g sample of propellant on a steam bath with 50 ml of distilled water for 20 min. Filter and wash the propellant residue on filter paper. Collect the filtrate and washings in a 250 ml volumetric flask and make up to the mark with distilled water.

**Procedure**—Zero the instrument galvanometer with the dark current knob and rinse a sample cup 3 times with the diluted standard. Then zero the galvanometer with the sensitivity knob with per cent of transmittance at 50.0 the shutter open and the diluted standard being atomized. Rock the wavelength dial to obtain the transmittance peak near 768  $m\mu$  and again zero the galvanometer at this peak with the sensitivity knob. Use the sample solution to rinse a sample cup 3 times and then introduce the sample into the atomizer. Using the per cent transmittance setting required to restore the galvanometer to zero read the percentage of  $KNO_3$  by

reference to the standard graph. Run the 50.0% transmittance standard between samples.

**For Sodium (Na) and Calcium (Ca).**—For sodium the wavelength is 589 m $\mu$ , slit is about 0.03 mm., and sensitivity is at number 2; for calcium the wavelength is 622 m $\mu$ , slit is about 0.05 mm., and sensitivity is at number 3.

**Standards.**—Prepare the concentrated standard for sodium and calcium by diluting 5.899 g. of potassium chloride (KCl), 0.658 g. of sodium chloride (NaCl), 8.000 g. of calcium carbonate (CaCO<sub>3</sub>), and 160 ml. of concentrated HCl to 2 l. in a volumetric flask. Dilute a 50-ml. aliquot of this solution to 1 liter (corresponding to 0.05% sodium sulfate and 0.50% calcium carbonate in a 10-g. sample). Prepare standard graphs using suitable dilutions of the concentrate.

**Sample.**—Digest a 10-g. sample of propellant in 20 ml. of concentrated HNO<sub>3</sub> in a 250-ml. Vycor beaker covered with a watch glass. Evaporate the residue, wipe the cover glass with ashless filter paper, add the paper and scavenged material to the residue, and heat the beaker and contents in a muffle furnace until all carbonaceous matter is oxidized. Add 3 ml. of concentrated HCl and 10 ml. of distilled water to the cooled beaker. Quantitatively transfer the solution to a 250-ml. volumetric flask through a filter paper, make the solution up to the mark, and mix.

Make exact wavelength and 50.0% transmittance settings and determinations in the same manner as given above for potassium.

#### CARBON BLACK BY PHOTOMETRIC OR SPECTROPHOTOMETRIC METHOD

This method for carbon black is valid in the presence of 2-nitrodiphenylamine.

**Reagent.**—Acetic acid-acetone solution; 5% glacial acetic acid in reagent acetone.

**Standard Graph.**—The standard carbon black material (complying with the requirements of the specifications for carbon black used in manufacturing the propellant) is dried in an oven at 105°C. for 2 hr. and then cooled in a desiccator for 30 min. A 0.1-g. portion is transferred to a disintegrator (such as the Waring Blender), and 100 ml. of acetic acid-acetone solution are added. After thorough dispersion in the disintegrator, the solution is transferred to a 1-liter volumetric flask and made up to volume with acetic acid-acetone solution. A Gooch or Selas crucible is prepared with an asbestos mat  $\frac{1}{4}$ -in. thick. The filter is washed with 10 to 15 ml. of 35% HNO<sub>3</sub> (1:1) then with warm water, dried at 100°C. for 1 hr., ignited, cooled in a desiccator, and weighed. Using very gentle suction, a 250-ml. aliquot of the carbon black dispersion is filtered through the crucible. Care is taken not to allow the crucible to run dry until all the solution is filtered. The crucible is dried by suction and then at 105°C. for 30 min., cooled in a desiccator, and weighed. This operation gives the gravimetric determination of carbon black in the dispersion. With this dispersion, a standard graph is made by placing pipetted aliquots in several (at least 4) 100-ml. volumetric flasks, and adding a total of 3 g. of all the propellant components (except the carbon black) in the proportion required by the formulation. Each flask is filled to about 95 ml. with acetic acid-acetone and shaken on a wrist-action shaker to thorough dissolution of the ingredients. Each flask is made up to the 100-ml. mark and the contents are mixed. The zero of a photometer is adjusted with acetic acid-acetone as a blank in a 1-cm. cell, and with a 540 m $\mu$  filter. With the same cell or a matching one, the transmittance of each of the synthetic standards is determined and the standard curve is plotted on linear graph paper. Alternatively, a Beckman DU spectropho-

tometer may be used with acetic acid acetone in the reference cell and a specific wavelength setting at 540 m $\mu$  or above (up to 700 m $\mu$ )

*Procedure for the Sample*—Three g of a finely divided (Wiley milled through 20 mesh) sample in a 100 ml volumetric flask are dampened with 5 ml of ethanol and 90 ml of the acetic acid acetone solution are added. After dissolution and making up to volume as for the standards the transmittance of the sample is measured in a 1 cm cell with acetic acid acetone as reference. From the dial readings and the standard curves the percentage of carbon black in the propellant is calculated. For propellants containing more than 0.1% carbon black a further dilution of the 3 g sample in 100 ml of solution is necessary.

#### CARBON BLACK, GRAVIMETRIC (NO GRAPHITE PRESENT)

*Procedure*—Prepare a Gooch or Selaas crucible with a  $\frac{1}{4}$  in asbestos mat. Wash the mat with 10 to 15 ml of 35%  $\text{HNO}_3$  (1:1) solution, rinse thoroughly with distilled water, dry in an oven and ignite at 600° to 650°C.

Treat a 5-g sample of propellant with 75 ml of 35%  $\text{HNO}_3$  in a 400 ml beaker covered with a watch glass. Heat gently at first on a steam bath, removing the beaker if reaction is too rapid. Digest on the steam bath for about 1 hr. Then chill the beaker in an ice bath. Add 75 ml distilled water, let stand until most of the carbon black has settled and filter with very gentle suction through the crucible. Do not allow the solution level to drop below the surface of the mat until filtration is completed. Rinse the beaker with distilled water and transfer all the carbon black to the crucible. Finally wash with hot distilled water and discard all the filtrate.

*Caution*—Nitric acid and acetone must not be allowed to come together as a violent reaction could ensue.

Wash the crucible thoroughly with acetone (absence of color in filtrate), dry the crucible by aspiration and then in the oven for 30 min at 275°  $\pm$  25°C. Cool the crucible in a desiccator and weigh it. Then ignite it at 600° to 650°C until all carbonaceous matter is removed. Cool in a desiccator and reweigh. Calculate loss on ignition to percentage of carbon black.

#### CARBON BLACK AND GRAPHITE GRAVIMETRIC

When the propellant contains both carbon black and graphite the procedure given above for carbon black alone is modified as follows.

*Procedure*—Digest a 5 to 10 g sample in the manner previously described, filter it through an acid washed crucible and wash thoroughly with hot water. *Discard the filtrate.* (*Caution*—Avoid mixing nitric acid and acetone.) Then wash thoroughly with acetone (absence of color in filtrate), dry by aspiration and then at 120° to 130°C, cool in a desiccator and weigh. Then ignite at 600° to 650°C, cool and reweigh. This step gives the value for carbon black and graphite together.

Treat a second 5 to 10 g sample in a 300 ml Erlenmeyer flask having a ST neck with 75 ml of 35% nitric acid on the steam bath heating as previously described. Then add an additional 50 ml of 35% nitric acid and reflux for 3 hr. (This refluxing step oxidizes the carbon black but not the graphite.) Filter as before through a crucible, wash with hot water and *discard the filtrate.* Wash thoroughly with acetone, dry by aspiration and then in an oven at 120° to 130°C. Cool in a desiccator and weigh. Then ignite at 600° to 650°C until all carbonaceous matter is removed. This step provides a measure of the graphite content.

Then calculate carbon black from the difference between the 2 determinations described.

### CELLULOSE ACETATE<sup>31</sup>

Cellulose acetate is sometimes used in double-base propellant as a burning rate modifier. The procedure given here for determining cellulose acetate is based on the phenomenon that, in alkaline media, cellulose acetate hydrolyzes to cellulose, while cellulose nitrate decomposes to a number of water-soluble products.

**Hydrolysis Solution.**—The hydrolysis solution is  $0.45 \pm 0.05$  *N* KOH in approximately 49% by volume of diethyl ether, 46% of ethanol, and 5% of water. This solution is prepared by adding  $42 \pm 2$  ml. of saturated aqueous KOH to 640 ml. of 95% ethanol. After mixing, it is diluted with 640 ml. (1 lb.) of diethyl ether, mixed, and poured through a rapid filter paper into a storage bottle. The normality of the resulting hydrolysis solution is determined by titration against a standard acid solution.

**Basic Procedure.**—Four g. of 20-mesh sample are weighed and transferred to a 300-ml. iodine flask having a 24/40 ST joint. Through a powder funnel, 250 ml. of the hydrolysis solution are added. The flask is stoppered with a No. 22 glass stopper, and covered with a small inverted cup to allow controlled pressure release. After standing a minimum of 15 hr., a few drops of phenolphthalein are added, and the solution is made slightly acidic with acetic acid to prevent any attack on the Alundum thimble.

An Alundum extraction thimble, unless previously used in this procedure, is pretreated with 50% acetic acid. The thimble (30 by 80 mm., flat bottomed, porosity RA98) is heated for 30 min. at  $725 \pm 25^\circ\text{C}$ ., cooled to room temperature in a desiccator, and weighed in a covered weighing bottle. One end of a 40-mm. length of Gooch rubber tubing is slipped over the top of the thimble for 10 mm. below the top edge. The thimble is placed in a filter tube, which is connected to a suction flask through a rubber stopper, and the other end of the tubing is stretched over the outside of the filter tube. Sufficient tubing is retained between the thimble and the filter tube so that it is convex when viewed from above. The insertion of the stem of a powder funnel into the top of the thimble completes the filtration assembly.

Most of the solvent is decanted through the funnel into the thimble from the residue and the dark lower liquid phase. To the residue in the flask, 60 ml. of hot 50% acetic acid are added. The solution is gently boiled for 6 min., with occasional swirling. The flask is cooled to a convenient temperature, and its contents are quantitatively transferred to the thimble using 50% acetic acid at  $40^\circ$  to  $60^\circ\text{C}$ . The funnel is removed, and the residue and the walls of the thimble are washed thoroughly with acetone, with some acetone passing between the outside of the thimble and the Gooch tubing, to wash the inside of the filter tube.

After suction drying, the thimble is placed in a vacuum oven at  $100^\circ \pm 5^\circ\text{C}$ . for a minimum of 3 hr. at a maximum absolute pressure of 40 mm. The thimble is placed in an uncovered weighing bottle (previously tared with its cover) and cooled to room temperature in a vacuum desiccator containing phosphorus pentoxide, and equipped with a drying tube at the inlet. The covered weighing bottle containing the thimble and the residue is reweighed.

<sup>31</sup> Based on the method of Fletcher, A. N., et al., *Anal. Chem.*, **31**, 1224, 1959.



**Insolubles Correction Procedure**—For very precise results a correction should be made for the insoluble impurities that may be present in the cellulose nitrate used to prepare the propellant. A military specification JAN N 244 for nitrocellulose allows up to 0.4% acetone insolubles in cellulose nitrate. Consequently an appreciable positive error could occur if a correction were not made for these impurities. If the cellulose nitrate used to manufacture the propellant is available the basic procedure is applied to a dried 5 g sample of this material to determine the correction value.

**Ash Correction Procedure**—If such a sample of cellulose nitrate is not available a less accurate corrective procedure may be followed. After using the basic procedure the thimble and contents are placed in a muffle furnace at 725°C for 30 min. The thimble is cooled in a desiccator to room temperature and weighed in the covered weighing bottle.

Calculations

$$\text{Cellulose acetate per cent} = \frac{100CG}{S}$$

where  $C$  = weight of cellulose in grams

$G$  = gravimetric conversion factor, and

$S$  = weight of sample in grams

The gravimetric conversion factor  $G$  may be calculated from the nominal percentage of acetyl content of the cellulose acetate by the formula

$$G = \frac{\text{weight of cellulose acetate}}{\text{weight of cellulose}} = \frac{4304}{4304 - (42.04 \times \text{percentage of acetyl})}$$

The gravimetric conversion factor  $G$  may also be obtained from the latter equation by a direct determination upon the cellulose acetate used in preparing the propellant. The basic procedure is followed except that a sample of about 2 g of dry cellulose acetate is taken and the cellulose is dried overnight before being weighed.

The weight of cellulose  $C$  is obtained in the following manner

Basic procedure

$$C = B - A$$

Insolubles correction procedure

$$C = B - A - NI$$

Ash correction procedure,

$$C = B - A'$$

where  $A$  = initial weight of thimble and weighing bottle,

$A'$  = weight of thimble and weighing bottle after 30 min ignition,

$B$  = weight of hydrolysis product, thimble and weighing bottle,

$I$  = fraction of insolubles found in cellulose nitrate, and

$N$  = nominal fraction of cellulose nitrate in sample

There are 3 semicritical steps in the basic procedure. First there must be sufficient KOH to react with the acidic products of the hydrolysis. Each gram of

propellant consumes about 1 g. of KOH. Consequently, at least 60 ml. of the hydrolysis solution should be used per gram of propellant. Whether sufficient alkaline solution was taken is checked just before the solution is acidified after the 15-hr. reaction period. The solution should turn red upon the addition of phenolphthalein. On the other hand, a large excess of hydrolysis solution should be avoided. Two phases are present at the end of the reaction. The lower phase, in contact with the cellulose, has a higher concentration of base than the upper. It is possible, consequently, for the hydroxide concentration in the lower phase to be undesirably high so that the glucoside chain of the cellulose would be attacked by the excess base present after hydrolysis.

The second semicritical step is in the washing procedure. Washing must be thorough, especially if the solution being filtered comes in contact with the portions of the walls that are in contact with the Gooch rubber tubing. Because this area is above the suction line, it is more difficult to wash it adequately.

Obtaining and keeping the cellulose in a dry state is the third operation requiring care. Cellulose should be treated in about the same manner as phosphorus pentoxide in regard to exposure to the atmosphere.

#### CYCLOTRIMETHYLENETRINITRAMINE, RDX, GRAVIMETRIC METHOD

Cyclotrimethylenetrinitramine (RDX, cyclonite, or hexogen) is determined in certain types of propellants by a simple extraction and gravimetric procedure. In addition to the RDX, a typical propellant may contain nitrocellulose, nitroglycerin, dibutyl phthalate, triacetin, and 2-nitrodiphenylamine.

*Procedure.*—A 5-g. sample is extracted with pentane-methylene chloride (2:1) azeotrope in a Soxhlet assembly heated by a water bath (*not a hot plate*). The extraction is continued for 6 to 8 hr. after all red or yellow color appears to have been removed from the thimble, care being taken to add additional *n*-pentane (not azeotrope) if solvent loss during extraction is discernible. (Discard this extract, insofar as the RDX determination is concerned.) After drying of the residue, thimble, and Soxhlet equipment, the residue is extracted with 95% ethanol, using a hot plate or heating mantle, but being extremely careful not to let the solvent volume decrease appreciably. The extract is quantitatively transferred to a tared evaporating dish, and the solvent is removed by evaporation on a steam or hot water bath, with the aid of a dry-air jet. The dish is then dried in an oven at 70°C. for 2 hr., cooled in a desiccator, and weighed. *Caution.*—The residue in the dish is RDX, and is highly explosive and sensitive. Large crystals are especially hazardous. Handle with great care and with protective devices (shields, safety glasses, etc.).

The increase in weight of the tared dish is used to calculate the percentage of RDX in the sample taken for analysis.

The residue from the alcohol extraction may be weighed (a fritted-glass thimble is used in the extraction if this determination is desired) and considered to be nitrocellulose.

The pentane-methylene chloride extract from the first extraction or a duplicate one may be used for determination of nitroglycerin, 2-nitrodiphenylamine, triacetin, and dibutyl phthalate by procedures described elsewhere under each of these ingredient headings.

## DIBUTYL PHTHALATE

See 'Phthalate Esters,' p 1396

DIETHYL PHTHALATE BY AZEOTROPIC DISTILLATION<sup>32</sup>

See also 'Phthalate Esters' p 1396

Although the azeotropic method is tedious, it has been demonstrated to be a reliable and accurate method for diethyl phthalate in propellants containing in addition to the phthalate, nitrocellulose, nitroglycerin, 2 nitrodiphenylamine, potassium sulfate, carbon black and lead stearate

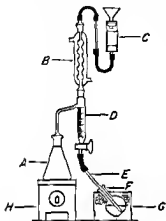


FIG 32 13 Azeotropic Distillation Apparatus A, Erlenmeyer Flask 500 ml, B, Condenser Water Cooled 400 mm C Water Trap D, Distillation Receiving Tube 25 ml at Top Graduation E Extension Tube F, Volumetric Flask 250 ml G Ice Water Bath H, Hot Plate 3 Heat

**Procedure**—Place a sample of finely divided propellant that contains about 0.3 g of diethyl phthalate in a 500 ml Erlenmeyer flask (with ST neck), and add a few carborundum chips and 50 to 100 ml of 30% KOH. Use 100 ml for propellants containing up to 5% DEP and 50 ml for propellants containing more than 5%. (The larger amount of hydroxide is needed for low content of phthalate because the larger sample required contains more nitrocellulose and nitroglycerin which also consume alkali.) Swirl the flask thoroughly to wet all the propellant and disperse clumps of sample.

**Caution**—In the heating step to follow local overheating of unwetted or clumped propellant can lead to explosion. A shield is recommended especially in the early stages of heating.

Assemble the apparatus illustrated in Fig 32 13. Connect the flask directly to the condenser (using a small amount of high melting stopcock grease). The receiving apparatus components (D, E, F, and G of Fig 32 13) are not connected at this stage. Attach the water trap C to the condenser, and pour 10 to 15 ml

of distilled water into it. With an electric hot plate, heat gently at first and then reflux at a moderate rate for 30 min. Remove the hot plate and allow the flask to cool for 10 min.

Detach the water trap, pour 25 ml of hydrogen peroxide (3% reagent) into the top of the condenser, and replace the water trap. Raise the trap to cause the water from the trap to rinse the peroxide into the flask, and refill the trap with water. Reflux gently for 60 min, remove the heat source, and cool the flask in cold water. Pour 50 ml of distilled water through the water trap into the condenser and flask.

Prepare ice bath, G, and assemble the distillation receiving equipment (D, E, F, and G). Detach the water trap, and pour 50 ml of benzene through the condenser and into receiver, D, and flask, A. Add just enough distilled water through the condenser to displace the benzene in the receiver, causing it to flow back into the flask. By opening the stopcock, drain all but 2.0 ml of the water from the

<sup>32</sup> Modification of the procedure described by Butts, P. G., Prince, G. B., Kouba, D. L., and Becker, W. W., *Anal Chem.* 20, 1066 (1948).

receiver, *D*, into the flask, *F*. No benzene must be allowed to enter flask, *F*. Replace the water trap. Heat the flask, *A*, to bring the contents to boiling (very gently at first). As distillation proceeds draw off 10 to 15 ml. aliquots of alcohol (produced by oxidation of the phthalate) and water until a total of 85 ml. has been collected in flask, *F*. (At no time during these operations draw down below the 5 ml. mark.) Remove the hot plate and disconnect the water trap, saving the water in the trap for a later step. Drain the last of the water from the receiver tube into the receiving flask, closing the stopcock when the benzene layer reaches the 0.2 ml. mark on the tube. Wash the benzene remaining in the tube with five 5-ml. portions of distilled water added through the condenser, drawing off each portion to the receiving flask. Disconnect tube *E* from the graduated tube, *D*, and pour a little water through tube *E* into the volumetric flask. Transfer the water from the water trap to the flask, rinsing twice with small portions of distilled water.

Remove the receiving flask from the ice bath, allow it to warm to room temperature, and fill to the mark (250-ml.) with distilled water.

Pipet a 50-ml. aliquot of the ethanol-water solution to a 250-ml. iodine flask, and add accurately 25.00 ml. of 0.2 *N* potassium dichromate solution. Close the flask loosely with a water-moistened glass stopper. Heat the flask on a steam bath for 75 min.; then cool it to room temperature. Add 15 ml. of 15% potassium iodide solution, swirl, and let stand a few minutes. Titrate with 0.1 *N* sodium thiosulfate solution using starch indicator.

Make a blank determination on a synthetic propellant sample containing all the ingredients of the sample except the phthalate.

$$\text{Diethyl phthalate, per cent} = \frac{2.778(A - B)N}{W_1} - \frac{2.778(A - C)N}{W_2}$$

where *A* = sodium thiosulfate to titrate iodine liberated from  $\text{KI}$  solution by exactly 25.00 ml. of 0.1 *N* potassium dichromate solution in milliliters,

*B* = sodium thiosulfate to titrate iodine liberated from  $\text{KI}$  solution by the potassium dichromate remaining after oxidation of the alcohol in the 50-ml. aliquot of distillate in milliliters,

*C* = sodium thiosulfate solution required by the blank in milliliters,

*N* = normality of sodium thiosulfate solution,

$W_1$  = weight of propellant sample, grams in the aliquot, and

$W_2$  = weight of synthetic sample, grams in the aliquot.

### DIMETHYL PHTHALATE

See "Phthalate Esters," p. 1396.

### DINITROTOLUENE BY TITANOUS CHLORIDE REDUCTION<sup>33</sup>

*Method When Nitrate Esters Are Not Present in the propellant.* Reagents. *Titanous Chloride Solution*, 0.2 *N*.—Same as for Nitroglycerin, p. 1392.

*Ferric Ammonium Sulfate*, 0.15 *N*.—Same as for Nitroguanidine, p. 1394.

*Procedure.*—A 5-g. sample is extracted with methylene chloride, the volatile solvent is removed by evaporation (air jet), the residue is taken up in glacial acetic acid, and made up to volume with this reagent in a 250-ml. volumetric flask. Inert gas ( $\text{CO}_2$  or  $\text{N}_2$ ) is passed through a special titration flask (Fig. 32-14) for

<sup>33</sup> Based on the method described by Becker, W. W., *Anal. Chem.*, 5, 152, 1933.

5 min before adding the sample and throughout the remainder of the determination. A 25 ml aliquot of the extract is pipetted to the titration flask and 0.2 N titanous solution is measured in from a buret using 4 ml of the standard reagent for each 1% of dinitrotoluene in the propellant (as known from the formulation value or a preliminary determination). Then 25 ml of 15% hydrochloric acid and a few glass beads or carborundum chips are added and the flask is connected to the reflux condenser. By means of an electric hot plate the solution is brought

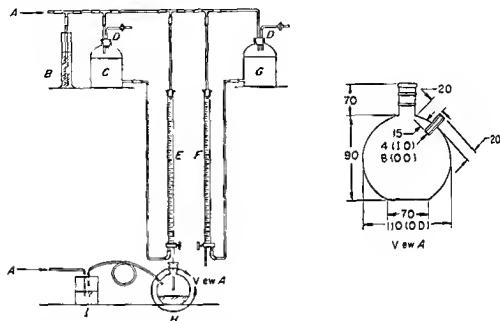


FIG. 32-11. Ferrous Titanous Titration Apparatus. A Inert Gas Supply (e.g. CO) B Pressure Relief Bubbler C Titanous Solution Storage Bottle D 2-Way Stopcock E Titanous Solution Buret F Ferrous Solution Buret G Ferrous Solution Storage Bottle H Titration Flask I Blubber for Rate of Flow Observation View A (All Dimensions in Millimeters)

to boiling and then refluxed for 5 to 10 min. Without disconnecting the condenser and with slightly increased gas flow the heat source is removed and the flask is cooled with a cold water bath. The condenser is disconnected and the flask contents are titrated with 0.15 N ferric ammonium sulfate using 5 ml of 20% ammonium thiocyanate as indicator. A reagent blank is made following the determination operations to give the ferric ammonium sulfate required by the same quantity of titanous solution as that used with the sample.

$$\text{Dinitrotoluene per cent} = \frac{1.518 \times (B - A)}{W} \quad (\text{See Eq. 32-3})$$

where  $W$  = grams sample represented by the aliquot

**Method When Nitrate Esters (e.g., Nitroglycerin) Are Present in the Propellant**—The sample is extracted in the same manner as described above and made up to volume in glacial acetic acid after removal of the volatile solvent. The nitrate ester is determined in accordance with the procedure given for Nitroglycerin.

p. 1391. The reduction with excess titanous solution described above is then applied immediately to the solution remaining in the titration flask at the end of the titration of ferric ion by titanous solution.

#### DIPHENYLAMINE BY TITRIMETRIC BROMINATION METHOD

The titrimetric bromination method is applied to single-base and double-base propellants containing no brominatable materials (such as salicylates, phenols, or centralites) other than diphenylamine.

**Procedure.**—Extract a 5-g. sample of propellant with volatile solvent (methylene chloride), evaporate the solvent (air jet), and take up the residue in 10 to 15 ml. of glacial acetic acid. For propellants containing less than 0.5% diphenylamine, quantitatively transfer this entire sample to a 250-ml. iodine titration flask, using glacial acetic acid as rinse liquid in a sufficient amount to make about 50 ml. of total liquid. For propellants containing 0.5 to 1.0% diphenylamine use an aliquot of half the sample (volumetric flask and pipet), and for propellants with more than 1.0% use a quarter of the sample.

Add from a buret 25 ml. of 0.2 *N* potassium bromate-bromide solution (5.6 g. potassium bromate and 30 g. potassium bromide per liter). Moisten the stopper of the flask with 1 or 2 drops of 15% potassium iodide solution, add 5 ml. of concentrated HCl to the flask, stopper the flask immediately, note the time, swirl the flask contents for a few seconds, and allow reaction to proceed for 60 to 75 sec. from the time noted. Add 10 ml. of 15% potassium iodide solution to the flask, and swirl the contents. Wash down the gallery and inner walls of the flask with distilled water, and titrate the solution with 0.1 *N* sodium thiosulfate with 5 ml. of starch solution added near the end of the titration.

Make a blank determination on the reagents using exactly the same amount of standard bromate-bromide solution as for the determination.

$$\text{Diphenylamine, per cent} = \frac{2.115N(B - A)}{W} \quad (\text{See Eq. 32-3.})$$

where *W* = grams sample in aliquot.

#### ETHYL CENTRALITE BY TITRIMETRIC BROMINATION METHOD

Determine ethyl centralite in exactly the same manner as the bromination method for determining diphenylamine, above, with the following exceptions.

Use the entire extract from a 5-g. sample when the propellant contains less than 4% ethyl centralite. For contents of 4 to 6%, and for above 6% use aliquots of one-half and one-quarter the sample, respectively.

$$\text{Ethyl centralite, per cent} = \frac{6.71N(B - A)}{W} \quad (\text{See Eq. 32-3.})$$

where *W* = grams sample in aliquot.

#### GRAPHITE

See Carbon and Tin and Graphite.

#### INFRARED PROCEDURES; ANALYSIS OF PROPELLANTS BY INFRARED SPECTROPHOTOMETRY

Single-beam and double-beam infrared spectrophotometers are advantageous in the analysis of propellants for a number of ingredients. Usually a cell in-cell out

technique is used for single beam work, and a compensating technique, for double beam. The composition of the propellant must always be considered in choosing appropriate wavelengths for the measurements of absorptions, and in making suitable deductions (corrections in single beam operations) or compensations (double beam) for interfering substances. A procedure typical of each technique is given below. Both of these examples are for a single base propellant with the following nominal composition: NC 84%, DNT, 10%, DBP, 5%, DPA 1%.

In each case a Soxhlet extraction with methylene chloride as solvent is made which removes the soluble components from the NC and other insoluble ingredients. The extraction time depends on the type of the sample and must be predetermined on typical material. Periods ranging from 6 to 24 hr have been used. See remarks under Solvent Extraction, p 1372.

**Single Beam, Cell In Cell Out Procedure.** Determination of DBP.—Evaporate the solvent from the methylene chloride extraction of 4 000 g of propellant by means of a stream of dry air and very moderate heat. Dry only to solvent dryness. Faint traces of residual methylene chloride will not interfere. The first stage of the evaporation is performed in a flask or beaker, the final stage in a tared, 25 ml, screw cap vial. Then dilute the contents of the vial to 10 000 g with ethylene chloride, cap the vial and shake it to mix the contents. Using a 0.1 mm cell with sodium chloride or calcium fluoride windows, measure the infrared absorbance at the peak of the  $5.75 \mu$  band.

At the same position, make absorbance measurements with the same cell and instrument settings for the empty cell, the solvent, and each of the other ingredients having some absorbance at that wavelength (DNT and DPA) using for these ingredients solutions containing the amounts extractable from the 4 000 g sample of the propellant.

Obtain net absorbance for DBP by subtracting absorbances due to cell, solvent, DNT, and DPA from the total absorbance of the propellant extract. Calculate the percentage of DBP in the ethylene chloride by means of a standard working curve of absorbance versus concentration prepared by measuring absorbances for DBP on 5 or more solutions spread over the range 0.5 to 2.5%. Convert the percentage of DBP value read from this curve to percentage of DBP in the propellant by multiplying by 2.5 (because the extract from 4 g of propellant was diluted to a total weight of 10 g).

As a rough guide typical absorbances at  $5.75 \mu$  corresponding to 1% of ingredient are: DBP, 0.3; DNT, 0.002; DPA, 0.006. For the cell plus solvent a typical absorbance is 0.72.

For a Beckman IR 2 single beam instrument typical settings are: slit, 0.38 mm, grating, 1, period, 2 sec, shutter, metal.

**Determination of DNT.**—The DNT is determined in much the same manner as that given above for DBP. The exceptions are as follows: the residue from evaporation of the methylene chloride extract of 4 000 g sample is diluted to 8 000 g (ratio 1:2), absorption is measured at the peak of the  $11.9 \mu$  band, the standard working curve is based on a series of DNT solutions covering the range 1.0 to 6.0%, and corrections are made for absorbances of cell, solvent, DBP, and DPA.

**Double Beam (Compensation) Procedure.** For DBP and DNT. *Reference Solution*—Dissolve a weighed quantity of DPA corresponding to the DPA content of a 5 g sample of propellant (i.e., 0.050 g for propellant containing 1%) in chloroform, and dilute to 500 ml.

*Calibration Solution.*—Dissolve 0.050 g. DPA, 0.250 g. DBP, and 0.500 g. DNT in chloroform, and dilute to 50.0 ml. (These quantities are based on the amounts, in a 5-g. sample, of propellant having the composition 1% DPA, 5% DBP, 10% DNT.)

*Calibration.*—Fill the thinner of 2 closely matched 0.2-mm. cells with reference solution, and the other with calibration solution, rinsing each cell several times with the solution introduced. Place the reference solution in the reference beam and the calibration solution in the sample beam of the spectrophotometer. Accurately set the 0% and 100% transmission at the 5.0  $\mu$  wavelength, then scan to 6.7  $\mu$ , using absorbance chart paper. Read absorbance of DBP at the peak of the band at about 5.8  $\mu$ , and the absorbance of DNT at the peak of about 6.55  $\mu$ . Calculate calibration constants for DBP and DNT as follows:

$$K_{(\text{DBP})} = \frac{A(\text{at } 5.8 \mu)}{0.250}$$

$$K_{(\text{DNT})} = \frac{A(\text{at } 6.55 \mu)}{0.500}$$

where  $K$  = calibration constant =  $\frac{A}{C}$ ,

$A$  = absorbance, and

$C$  = concentration.

*Analysis of Sample.*—Dry to solvent dryness the methylene chloride extract from a 5-g. sample, using a stream of dry air and very moderate heat. Avoid overheating. Quantitatively transfer this residue to a 50-ml. volumetric flask using chloroform as solvent, and make up to the mark. Using the same techniques and settings as for calibration, scan the sample solution from 5.0 to 6.7  $\mu$ , and read the peak absorbances at the 5.8 and 6.55  $\mu$  locations.

$$\text{DBP, per cent} = \frac{100(A \text{ at } 5.8 \mu)}{K_{(\text{DBP})} \times (\text{weight sample})}$$

$$\text{DNT, per cent} = \frac{100(A \text{ at } 6.55 \mu)}{K_{(\text{DNT})} \times (\text{weight sample})}$$

*Instrument Settings.*—Typical settings for a Perkin-Elmer Model 21 spectrophotometer are: slit, 984  $\mu$  (schedule 2); response, 1:1; speed 4 (approx. 0.33  $\mu$  per min.) or slower; gain, as required for the specific instrument.

*Typical Procedures for Analysis of Double-Base Propellants.*—The detailed procedures described above are for a single-base formulation. Procedures for double-base formulations are very similar. Also DEP, DOP, and TA, in double-base propellants, are commonly determined by infrared techniques. These ingredients are usually extracted from a finely divided sample of the propellant with methylene chloride in a Soxhlet apparatus. The methylene chloride is then evaporated in the manner described above for determining DBP and DNT. Table 32-8 shows the essential procedural details for single-beam and double-beam operations, applied to 3 typical formulations.



TABLE 32-8 EXAMPLES OF INFRARED PROCEDURES APPLIED TO THREE DOUBLE-BASE FORMULATIONS

Nominal Formula, Per Cent	Case 1	Case 2	Case 3	
NC <sup>a</sup>	52	55	60	
NG	35	28	25	
DEP	11	—	—	
TA	—	15	10	
DOP	—	—	3	
2NDPA	2	—	2	
EC	—	2	—	
Ingredient determined	DEP	TA	TA	DOP
Ingredients compensated	NG, 2NDPA	NG, EC	NG, 2NDPA and DOP	NG, 2NDPA and TA
Single beam details				
Amount of sample in grams	1	1	1.5	6
Spectro solvent	ethylene chloride	ethylene chloride	benzene	chloroform
Total weight of sample and solvent in grams	10	20	15	10
Absorption measured at, $\mu$	5.8	5.8	8.2	8.9
Cell thickness in milli- meters	0.1	0.1	0.1	0.2
Double-beam details				
Amount of sample in grams	2.5	3	5	10
Spectro solvent	chloroform	chloroform	chloroform	chloroform
Total volume sample and solvent in millimeters	50	50	50	25
Absorption measured at, $\mu$	5.8	5.8	7.3	8.9
Cell thickness in milli- meters	0.2	0.2	0.2	0.2

<sup>a</sup> NC and other insolubles

## LEAD COMPOUNDS

Total lead from lead compounds in propellants may be determined in a variety of ways; of these, the sulfate procedure given here is simple and accurate.

*The Sulfate Method.*—A propellant sample of 5 to 20 g. (depending on lead content) is placed in a tall-form, 300-ml. beaker. Fifty ml. of 65 to 70% acetic acid, 20 ml. of concentrated  $\text{HNO}_3$ , and 10 to 15 ml. of concentrated  $\text{H}_2\text{SO}_4$  are added, in the order named, with swirling of the beaker contents. The beaker is covered with a ribbed cover glass, and heated on an electric hot plate at low heat until the more violent reaction stages are past. It is then heated until fumes of sulfur trioxide appear. The beaker is removed from the hot plate, cooled nearly to room temperature, 10 ml. of  $\text{HNO}_3$  are added, and heating is repeated. The cooling, addition of  $\text{HNO}_3$ , and reheating cycle is repeated until the residual  $\text{H}_2\text{SO}_4$  solution is colorless (or very pale yellow) when white fumes appear. Then heating is continued for 10 min. The beaker is cooled, and the cover glass and inner sides of the beaker are washed down (slowly at first to avoid excessive bubbling) with about 50 ml. of distilled water. The solution is then boiled for two min. (occasionally stirring or swirling may be necessary to avoid loss by bumping), and allowed to cool to room temperature. Fifteen to 20 ml. of 95% ethanol are added and the solution is allowed to stand at least 4 hr. (preferably overnight).

The solution is filtered through a tared Selas or Gooch crucible containing an asbestos pad, then the precipitate is transferred quantitatively to the crucible and washed with 3 *N*  $\text{H}_2\text{SO}_4$ . The precipitate is washed with 2 portions of 50% ethanol and 1 portion of 95% ethanol, dried first by suction and then at 105° to 110°C. for 15 to 30 min. It is ignited in a muffle furnace at 550° to 600°C. for 15 min., cooled in a desiccator, and weighed.

$$\text{Compound, per cent} = \frac{100AB}{nCW} = \frac{0.3297AB}{nW}$$

where *A* = weight of lead sulfate in grams,

*B* = molecular weight of lead compound in the propellant,

*n* = number of lead atoms in the compound,

*C* = molecular weight of lead sulfate (303.27), and

*W* = weight of sample taken for analysis in grams.

## NITROCELLULOSE, GRAVIMETRIC, BY ACETIC ACID EXTRACTION

The gravimetric acetic acid extraction method is suitable for the determination of nitrocellulose (cellulose nitrate) in many propellants. It is not applicable if the nitrogen content of the nitrocellulose is less than 12.2%. It is not appropriate also for propellants containing ingredients, other than the nitrocellulose, that are insoluble in acetic acid of the strength specified, unless the necessary correction can be obtained from an independent determination of the interfering substances.

*Procedure.*—A 3- to 5-g. sample of finely divided propellant is extracted with 65 to 70% w/w acetic acid in a 250- or 300-ml. Erlenmeyer flask having a ST neck. The sample is heated with 100 ml. of the acid, either for a minimum of 3 hr. on a steam bath with the flask loosely stoppered by a glass stopper, or by refluxing gently for 30 min. on an electric hot plate. The hot supernatant acid is decanted through a tared, sintered-glass crucible of medium porosity. The residue is then re-extracted with 50-ml. portions of 65 to 70% acid, using 3 portions and 3 reheating periods of 10 to 15 min. if the steam bath is used, or 1 portion with a

5 min period by the refluxing procedure. The residue is then quantitatively transferred to the crucible using a jet of hot distilled water. The crucible and contents are thoroughly washed with hot water, dried to constant weight in an oven at  $100^{\circ} \pm 5^{\circ}\text{C}$  or preferably, in a vacuum oven at  $60^{\circ}$  to  $70^{\circ}\text{C}$ , cooled in a desiccator, and weighed. The weight is considered constant when successive 1 hr periods of heating do not cause a loss in weight exceeding 3 mg. Calculate weight of residue to percentage of nitrocellulose.

#### NITROCELLULOSE BY FERROUS TITANOUS TITRATION<sup>34</sup>

The ferrous titanous method given here is the only satisfactory method known at present for determining nitrocellulose (cellulose nitrate) in propellants containing cellulose acetate and certain other ingredients insoluble in acetic acid. It is applicable to all types and grades of nitrocellulose wherever no other currently used method (including the nitrometer) has this universal validity.

**Reagents** *n* Butyl Acetate, Eastman Kodak Co. white label.

Ferrous Ammonium Sulfate Solution, Approximately 0.7 *N*—Same as for 'Nitroglycerin' p 1391.

*n* Hexane, Phillips Technical Grade, or Equivalent.

*n* Pentane, Phillips Technical Grade, or Equivalent.

Titanous Chloride, Standard Solution, 0.2 *N*—Same as for Nitroglycerin p 1392.

**Procedure**—Extract a finely divided (Wiley milled 20 mesh) sample of propellant that will yield 0.20 to 0.30 g of nitrocellulose with methylene chloride or 65 to 70% acetic acid to remove nitroglycerin and other soluble nitrate esters. Filter the residue onto a medium porosity fritted glass or Selas crucible, wash with methylene chloride if that solvent was used as extractant or with water if the acid was used, and dry the residue to constant weight in a vacuum oven at  $60^{\circ}$  to  $70^{\circ}\text{C}$ . Transfer the residue to a 300 or 500 ml reduction flask having a sealed-in arm for introduction of inert gas ( $\text{CO}_2$  or  $\text{N}_2$ ) and a ST neck (see Fig 32-14), using a powder funnel and a stream of *n* pentane *n* hexane solvent (3 l) from an all glass or polyethylene wash bottle. Rinse the funnel by pouring 45 ml of glacial acetic acid through it into the reduction flask. Add a few glass beads or carborundum chips to the flask. Remove most of the pentane hexane solvent by heating the flask for a few minutes on a steam bath. Add 25 ml of *n* butyl acetate to the flask and connect the stream of inert gas to the side arm. Connect the flask to a Graham type condenser and heat on an electric hot plate until the solution has boiled for 1 to 2 min. Cool the flask to approximately room temperature with a cold water bath.

Add rapidly 25 ml of 0.7 *N* ferrous ammonium sulfate solution from a buret having a coarse tip, and then add 8 to 10 ml of concentrated HCl from a dispensing buret. The amount of HCl is critical and must be kept within the prescribed limits. Reflux the flask contents until a series of color changes from light green to dark green to yellow occurs and then for 10 min longer. Usually a total of 30 to 40 minutes is required. Agitate the contents of the flask throughout the boiling at about 5 min intervals by hand shaking the flask. Cool the flask and contents in a cold water bath, loosen the condenser joint slightly and wash the condenser by pouring 30 ml of 65 to 70% acetic acid (oxygen free by  $\text{CO}_2$  sparging) into the top of the condenser. After a few minutes disconnect the flask from the condenser, and titrate the flask contents with 0.2 *N* standard titanous chloride solu-

<sup>34</sup> Procedure described by Pierson, R. H., and Julian, E. C., *Anal. Chem.*, **31**, 589, 1959.

tion, adding 5 ml. of 20% ammonium thiocyanate near the end. As the end point is approached, add titrant very slowly, with at least 10 sec. allowed between each drop added, and with good agitation. Complete discharge of red coloration marks the end point.

Make a blank determination on the reagents processed through all the determination steps.

$$\text{Nitrocellulose, per cent} = \frac{46.693(V - B)N}{PW} = \frac{F(V - B)N}{W}$$

where  $V$  = standard titanous solution used for the sample in milliliters,

$B$  = standard titanous solution used by the blank in milliliters,

$N$  = normality of standard titanous solution,

$P$  = percentage of nitrogen in the nitrocellulose used in manufacturing the propellant,

$W$  = sample weight in grams, and

$$F = \frac{46.693}{\text{percentage of nitrogen in the NC}}$$

## 2-NITRODIPHENYLAMINE BY SPECTROPHOTOMETRIC METHOD

**Preparation of Standard Curve.**—A 0.5000-g. sample of high purity 2-nitrodiphenylamine is dissolved in 100 ml. of 95% ethanol. From this stock solution 0.2 ml. increments in the range 1.0 ml. to 3.0 ml. (11 aliquots) are each made up to 100 ml. in volumetric flasks. Transmittance of each of these standards is measured at 430  $m\mu$  using a Beckman DU spectrophotometer (or equivalent) and 10-mm. Corex cells with 95% ethanol in the reference cell. The results are plotted on 1-cycle, semi-log paper with transmittance on the ordinate (log) scale and milligrams 2-nitrodiphenylamine on the abscissa (linear) scale.

**Procedure.**—A 0.5000-g. sample of finely divided propellant is placed in a 100-ml. round bottom flask and extracted for 30 min. by refluxing with 50 ml. of 95% ethanol. The solution is filtered through filter paper to a 100-ml. volumetric flask. The reflux flask and filter are rinsed with several small portions of hot ethanol. After cooling to room temperature, the volumetric flask is made up to volume with the 95% ethanol. Provided the propellant contains not more than 1.5% 2-nitrodiphenylamine, the transmittance of the solution prepared as just described is determined at 430  $m\mu$  in a 10-mm. cell, with 95% ethanol in a matched cell as reference. For propellants containing 1% of 2-nitrodiphenylamine the solution will give a transmittance of about 40 to 50%. For propellants containing more than 1.5% of 2-nitrodiphenylamine, a further suitable dilution with ethanol is made to bring the transmittance near the midrange of the standard curve. Percentage of 2-nitrodiphenylamine is calculated by reference to the standard curve, taking into account the sample weight taken and the final dilution used.

## NITROGLYCERIN (GLYCERYL TRINITRATE) BY FERROUS-TITANOUS TITRATION

**Reagents.** Ferrous Ammonium Sulfate, Approximately 0.7 *N*.—Prepare a solution containing 1100 g. of ferrous ammonium sulfate hexahydrate,  $\text{FeSO}_4(\text{NH}_4)_2 \cdot 6\text{H}_2\text{O}$ , and 560 ml. of concentrated  $\text{H}_2\text{SO}_4$  in 4000 ml. of solution (use oxygen-free distilled water). Reduce the ferric iron by treating the solution with powdered iron (reduced by hydrogen) until a drop produces no immediate pink color with

ammonium thiocyanate solution. Filter through a large folded filter paper. It is advisable to feed a current of carbon dioxide into the filtrate during filtration. Agitate the reagent with carbon dioxide for a few minutes and store under carbon dioxide.

Reduce and refilter whenever a 25 ml portion requires more than 0.2 ml of 0.2 N titanous chloride solution to reduce the ferric iron present.

**Titanous Chloride Standard Solution 0.2 N**—In a 2000 ml beaker warm 400 ml of 38% HCl to 70 to 80°C on a hot plate (HOOD). In small increments add 48 g of TiH, keeping the beaker covered except when additions are being made. When hydrogen evolution has nearly ceased, remove the beaker from the hot plate, cool to near room temperature, add 1000 ml of oxygen free distilled water (boiled and cooled or purged with inert gas) and mix the solution by passing into it a stream of oxygen free inert gas (CO or N). Filter the solution through filter paper until perfectly clear. Add 1000 ml of 38% HCl and dilute to 4000 ml with oxygen free distilled water. Agitate and store in a dark bottle under inert gas. See Fig. 32.14 which depicts a typical protective system.

Standardize as follows: pass inert gas (e.g., CO) through a special titration flask (Fig. 32.14) for 5 min and then continuously for the remainder of the determination; transfer to the flask an accurately weighed portion of  $K_2Cr_2O_7$  (Bureau of Standards sample No. 136 previously dried at 110°C) or an accurately measured volume of 0.2000 N standard dichromate solution; add 50 ml of 10%  $H_2SO_4$  solution and titrate with the 0.2 N titanous chloride solution, adding near the end point 4 to 5 drops of sodium diphenyl benzidine sulfonate (0.5 g in 100 ml of water) as indicator; the color change sequence of the indicator itself is dark brown or purple to blue to colorless; the final color of the titrated solution at the end point being the green due to chromic ion; at this point add 5 ml of 20% ammonium thiocyanate indicator and discharge the red color which appears if iron is present by an additional titration with the titanous solution until the green color is restored.

Calculate the normality of the titanous solution corrected for iron content as follows:

$$N \text{ (corrected)} = \frac{0.2D}{T} \text{ if exactly 0.2000 N dichromate solution was used}$$

or

$$N \text{ (corrected)} = \frac{A}{0.04904T} \text{ if solid dichromate was weighed}$$

where  $D$  = milliliters of the 0.2000 N solution of dichromate

$T$  = total milliliters of titanous solution (including amount required for iron and with temperature and buret corrections) and

$A$  = solid potassium dichromate in grams

**Preparation of Sample** For propellants containing nitrocellulose with a nitrogen content in excess of 12.2% extract with 65 to 70% acetic acid or with volatile solvent (methylene chloride). In the case of propellants containing nitrocellulose of less than 12.2% nitrogen make the extraction with the volatile solvent. (The acid solution cannot be used in this case because of its solvent action on the NC.) If the volatile solvent is used perform the extraction in a Soxhlet apparatus; evaporate the solvent using an air jet and take up the residue in glacial acetic acid.

When the 65 to 70% acetic acid is used as solvent, make the extraction by heating sample and solvent in a flask on a steam bath, or by refluxing as described under "Nitrocellulose, Gravimetric, by Acetic Acid Extraction," p. 1389. Then filter the solution directly to a volumetric flask through a very fast filter paper.

**Procedure.**—Make the extract, representing 3 to 5 g. of finely divided propellant, up to volume with glacial or 65 to 70% acetic acid in a 250-ml. volumetric flask. Acetic acid has a high coefficient of thermal expansion, hence, the solution must not be allowed to change temperature until all aliquots have been taken.

Pass a stream of inert gas ( $\text{CO}_2$  or  $\text{N}_2$ ) into a special titration flask through the side arm for 5 min., and maintain this protective stream throughout the remainder of the determination. By pipet, transfer an aliquot (25 or 50 ml., depending on the nitroglycerin content of the sample) to the titration flask, add 15 ml. of 0.7 *N* ferrous ammonium sulfate from a buret with a coarse tip, and add 25 ml. of 15% HCl from a dispensing buret. Add a few glass beads or carborundum chips to the flask, and connect it to a reflux condenser. Heat the flask contents by means of an electric hot plate. Boil the solution until the color becomes a golden yellow, and then boil for an additional 5 min. Usually 10 min. total boiling time is adequate. Cool the flask and contents in a cold-water bath, loosen the condenser joint slightly, and wash the condenser by pouring 30 ml. of 65 to 70% acetic acid (oxygen-free, by  $\text{CO}_2$  sparging) into its top. After a few minutes draining, disconnect the flask from the condenser, and titrate the flask contents with 0.2 *N* standard titanous chloride solution, adding 5 ml. of 20% ammonium thiocyanate near the end. As the end point is approached, add titrant very slowly with at least 10 sec. allowed between each drop added, and with good agitation. Complete discharge of red coloration marks the end point.

Make a blank determination on all the reagents processed through all the determination steps.

$$\text{Nitroglycerin, per cent} = \frac{2.523N(V - B)}{W} \quad (\text{See Eq. 32-1.})$$

where  $W$  = grams sample in the aliquot.

#### NITROGUANIDINE, BY WATER EXTRACTION

**Procedure.**—An accurately weighed 3- to 5-g. sample of finely divided propellant is placed in a 25 by 50 mm. extraction thimble, having a sintered-glass bottom of medium or coarse porosity, and is covered with a plug of borosilicate glass wool. The sample is then extracted with carbon tetrachloride or a pentane-methylene chloride (2:1) azeotrope using either a Wiley or Soxhlet apparatus. In the latter case it is advantageous to support the thimble off the bottom of the Soxhlet tube with a section of glass tubing so that the maximum liquid level before siphoning is about  $\frac{1}{2}$  to  $\frac{2}{3}$  the way below the top of the sintered-glass tube. A 4-hr. extraction period is usually adequate. It is advisable to use a drying tube on the condenser to prevent entry of atmospheric moisture. The thimble is removed from the extraction apparatus, allowed to drain, and dried for 1 hr. in an oven at 100° to 105°C. or in a vacuum oven at 60° to 70°C. The thimble is weighed, reheated, and reweighed at 1-hr. intervals until loss of weight between weighings is not greater than 3 mg. The nitroguanidine component is then extracted with hot water, either by pouring eight 200-ml. portions of *boiling* water through the thimble with the aid of gentle suction, or by extraction in a Wiley or Soxhlet apparatus. The

thimble is dried by suction then to constant weight by oven heating by one of the methods described above

$$\text{Nitroguanidine, per cent} = \frac{100(A - B)}{W} - C$$

where  $A$  = weight of thimble and contents prior to water extraction in grams

$B$  = weight of thimble and contents after water extraction in grams

$W$  = weight of sample in grams and

$C$  = correction percentage of water soluble constituents other than nitroguanidine (if any) contained in the propellant and determined by some suitable auxiliary test

### NITROGUANIDINE BY BUFFERED TITANOUS CHLORIDE REDUCTION<sup>25</sup>

**Reagents** Titanous Chloride 0.2 N Standard Solution Same as for Nitro-glycerin p 1392

**Ferric Ammonium Sulfate 0.15 N Standard Solution**—To 400 ml of distilled water add 7.5 g of reagent grade hydrated ferric ammonium sulfate  $\text{Fe}_2(\text{SO}_4)_3 \cdot (\text{NH}_4)_2 \text{SO}_4 \cdot 24\text{H}_2\text{O}$  and 25 ml of 95% w/w  $\text{H}_2\text{SO}_4$ . Stir dilute to 1000 ml with distilled water and filter through a fast filter paper. Standardize against freshly standardized 0.2 N titanous chloride using 5 ml of 20% w/v ammonium thiocyanate as indicator

**Buffer Solution**—A 1:1 (w/v) aqueous solution of sodium acetate trihydrate plus approximately 7 ml of 30% NaOH solution per 25 ml of sodium acetate solution to give a pH of  $11.5 \pm 0.5$

**Procedure**—Extract an accurately weighed sample of about 2 g of propellant with carbon tetrachloride or pentane-methylene chloride (2:1 by volume) azeotrope in a Wiley or Soxhlet apparatus using a 25 by 50 mm extraction thimble having a sintered glass bottom of medium or coarse porosity. After drying the residue transfer it to a beaker containing 200 ml of distilled water and boil for 15 min. Decant the solution through a rapid filter paper into a 500 ml volumetric flask. Repeat the boiling with hot water twice using 100 to 125 ml of water each time. Cool the solution to room temperature and make its volume to 500 ml. Displace the air from a special titration flask (either 300- or 500 ml capacity as in Fig 32.14) by a stream of carbon dioxide and maintain the protective gas flow throughout the remainder of the determination. Measure 50 ml of 0.2 N standard titanous solution into the titration flask from a buret add 25 ml of the buffer solution and then add from a pipet a 50 ml aliquot of the sample solution. This order of addition of solutions must not be altered. Stir the flask contents by a magnetic stirrer and add 25 ml of HCl (1:1) and 5 ml of 20% ammonium thiocyanate indicator solution. After 3 minutes back titrate the excess titanous solution with 0.15 N standard ferric ammonium sulfate solution

$$\text{Nitroguanidine per cent} = \frac{1.7345N(B - A)}{W} \quad (\text{See Eq 32.3})$$

where  $W$  = grams of sample in aliquot

<sup>25</sup> Based on the method described by Roth Milton and Wegman Raymond F Anal Chem 30, 2036 1958

*PENTAERYTHRITOL TRINITRATE AND NITROGLYCERIN  
BY POLAROGRAPHIC METHOD*<sup>36</sup>

This polarographic method is applicable to propellants that may contain nitrocellulose, 2-nitrodiphenylamine, and dibutyl phthalate, in addition to the pentaerythritol trinitrate and nitroglycerin.

*Apparatus.* Polarograph, Sargent Model XXI or Equivalent.

Spectrophotometer, Cary Model XI, Beckman DU or Equivalent.

*Dropping Mercury Electrode.*—The electrode should have a drop rate within the range 2 to 5 sec. per drop. The cell should be maintained at  $30^{\circ} \pm 0.2^{\circ}\text{C.}$ , and be provided with a mercury pool anode.

*Reagents.* Sodium Hydroxide Reagent.—Transfer 12.5 ml. of a 5 *N* aqueous sodium hydroxide solution to a 50-ml., glass-stoppered, volumetric flask, and dilute to the mark with 95% ethanol.

Tetramethylammonium Chloride.—Dissolve 27.65 g. of the solid reagent in 175 ml. of distilled water, transfer to a glass-stoppered 250-ml. volumetric flask, add 5 ml. of a 1 to 1000 methyl red solution, and dilute to volume with 95% ethanol.

*Standard Solutions of Propellant Ingredients.*—Make up standard solutions of nitroglycerin, pentaerythritol trinitrate, and 2-nitrodiphenylamine in appropriate concentrations in 95% ethanol so that aliquots of 0 to 5 ml. added to the 25-ml. reaction flask will cover the expected concentration ranges of the constituents in propellant samples.

*Procedure.*—Weigh a 0.5-g. sample of the propellant, transfer it to a 50-ml. glass-stoppered volumetric flask, and add approximately 25 ml. of acetone. Place the flask on a mechanical shaker or shake by hand until the sample dissolves. Dilute the sample to volume with acetone.

*Total Sample.*—Pipet a 5-ml. aliquot of the sample into a 25-ml. volumetric flask and dilute to volume with 95% ethanol. Pipet a 10-ml. aliquot of this solution into a 30-ml. polarographic beaker, add 10 ml. of the supporting electrolyte (tetramethylammonium chloride), stir the solution, flush with nitrogen (previously scrubbed with 70% ethanol) for 5 min., and polarograph. Determine a second polarogram immediately and average the wave heights of the 2 polarograms. The wave obtained at approximately  $-0.82$  volt (vs. mercury pool) is due to the nitroglycerin, 2-nitrodiphenylamine, and pentaerythritol trinitrate in the sample.

*Reacted Sample.*—Pipet a 5-ml. aliquot of the original sample into another 25-ml. flask and dilute almost to volume with 95% ethanol. Pipet a 1-ml. aliquot of the NaOH reagent into the flask, and dilute to volume with 95% ethanol. Shake the flask to ensure homogeneity, take a 10-ml. aliquot, and treat it in the same manner as the total sample. Polarograph the sample immediately after reaction, although the time is not critical. Again average 2 wave heights. The wave height at approximately  $-0.50$  volt (vs. mercury pool) is due to the 2-nitrodiphenylamine and the pentaerythritol trinitrate in the sample.

*Preparation of Standard Curve by Standard Addition Technique.*—Dissolve a 0.5-g. sample of the propellant in acetone as in the regular procedure, and pipet a series of 5-ml. aliquots into 25-ml. volumetric flasks. Make 6 series of standard addition solutions, 2 for each of the following ingredients: pentaerythritol trinitrate; nitroglycerin; and 2-nitrodiphenylamine, using 0.5 ml. of the standard ingredient solution added to the 5-ml. propellant solutions in the 25-ml. flasks.

<sup>36</sup> Based on the method described by Ayres, W. M., and Leonard, G. W., *Anal. Chem.*, 31, 1485, 1959.



Treat 1 series for each ingredient by the "total sample" procedure, the other series by the "reacted sample" procedure. No series is needed for dibutyl phthalate since it does not interfere in the determinations. Express wave heights as microamperes and correct for the presence of the propellant. Plot these wave heights against concentration to provide the standard working curves.

**Calculation of Results.**—Polarographic waves for pentaerythritol trinitrate, nitroglycerin, and 2 nitrodiphenylamine overlap. While the reaction with base destroys the nitroglycerin wave, the waves for both pentaerythritol trinitrate and 2 nitrodiphenylamine are shifted in potential but not destroyed. Hence, when 2 nitrodiphenylamine is present in the propellant sample being analyzed for nitroglycerin and pentaerythritol trinitrate, it is necessary to determine the 2 nitrodiphenylamine by an independent method (e.g., spectrophotometrically) and then apply a suitable correction to both the total and reacted wave heights. The amount of correction is obtained by reference to the standard polarographic curves of the 2 nitrodiphenylamine.

The pentaerythritol trinitrate content of the sample is found from the wave height of the reacted sample after correction for 2 nitrodiphenylamine. The nitroglycerin content is determined from the total sample wave height after correction for the 2 nitrodiphenylamine and pentaerythritol trinitrate present. Pentaerythritol tetranitrate, present in the trinitrate as impurity, will be included in the trinitrate determination values, since the polarographic method does not differentiate between the 2 compounds.

#### *PHTHALATE ESTERS BY GENERAL METHOD, GRAVIMETRIC OR TITRIMETRIC\**

The method described here is suitable for determination of dimethyl diethyl dibutyl, or dioctyl phthalate in propellants containing, in addition to the phthalate, nitroglycerin, nitrocellulose, dinitrotoluene, diphenylamine, 2 nitrodiphenylamine, ethyl centralite, and triacetin.

**Reagents.** Anhydrous Ethanolic Potassium Hydroxide, Approximately 0.5 N.—Prepared from "purified from ethanol grade KOH, and ethanol containing not more than 0.5% water.

Potassium Carbonate, 10% Solution.

Anhydrous Diethyl Ether-Ethanol (1:1 by vol.) Wash Solution—Maximum water content 0.25%.

Acetic Acid, Dilute, 65 to 70% by Volume.

Copper Sulfate, Saturated Solution in Water.

Crystal Violet Indicator, 0.1% in Glacial Acetic Acid.

Perchloric Acid, 0.1 N Standard Solution—Prepared by adding 9 ml of 70% perchloric acid drop by drop to 50 ml acetic anhydride kept chilled during preparation. The resulting solution is diluted with 720 ml of glacial acetic acid and aged for 2 weeks. It is standardized against potassium hydrogen phthalate in glacial acetic acid with crystal violet as indicator.

**Procedure, Gravimetric.**—An accurately weighed sample of about 2 g of propellant is placed in a small paper thimble, covered with a plug of glass wool, and

\* Based on the method described by Stalcup, Harry, McCollum, Frank, and Whitman, C. L., Anal. Chem., 29, 1479, 1957.

extracted with methylene chloride for 3 hr. in a Soxhlet apparatus with a 250-ml. refluxing flask. The methylene chloride is removed by evaporation (air jet), and 25 ml. of 65 to 70% acetic acid are added to the flask. The solution is heated to 70°C., a few drops of saturated copper sulfate are added, and the flask is stoppered and then swirled occasionally during a 15 min. period. During the 15-min. period, 5 g. of zinc dust are added in small portions.

The hot solution is filtered through a medium-porosity, fritted-glass Büchner funnel into a 500-ml. separatory funnel (preferably with Teflon stopcock) containing 250 ml. of water. The flask and filter are rinsed carefully with two 10-ml. portions of hot 65 to 70% acetic acid, and about 75 ml. of methylene chloride from a wash bottle. The separatory funnel is shaken for about 1 min., and the 2-phase mixture is allowed to separate. The lower layer (containing phthalate) is transferred to a 500-ml. Squibb-type separatory funnel (preferably with Teflon stopcock). Five ml. of additional methylene chloride are added to the first separatory funnel and, without shaking, the lower solvent layer is transferred to the second separatory funnel. The acetic acid in the first funnel is then extracted twice by shaking with 25-ml. portions of methylene chloride, these extracts being added to the second funnel. The acid in the first funnel is then discarded.

Fifty ml. of 10%  $K_2CO_3$  solution are then added to the second separatory funnel containing the combined methylene chloride extracts. The funnel is shaken vigorously to neutralize all acetic acid present in the methylene chloride. A test is made with indicator paper to make sure an excess of  $K_2CO_3$  is present. The methylene chloride is transferred to a 250-ml. iodine flask. The  $K_2CO_3$  solution is washed several times by shaking with 10-ml. portions of methylene chloride, care being taken at all times to lose none of the phthalate and to prevent any carbonate solution entering the iodine flask.

The methylene chloride in the iodine flask is evaporated on a steam bath with the aid of a small jet of dry air until no odor of the volatile solvent is detectable. The flask is immediately removed at this stage, and 25 ml. of 0.5 *N* KOH solution in anhydrous alcohol are added. The flask is loosely stoppered (glass) and heated in a water bath at 60° to 70°C. for 1 hr.

The stopper is removed, the flask is cooled to room temperature, and 25 ml. of dry diethyl ether are added. The contents of the flask are filtered by suction through a medium-porosity, fritted-glass crucible, which has been previously weighed, inside a tared, stoppered, weighing bottle. The crucible is washed with absolute diethyl ether-ethanol (1:1). Except at the end of filtration, the precipitate should not be drained dry of solvent, because atmospheric moisture can dissolve some of the phthalate salt. Completion of removal of KOH by the washing process is tested for with a drop of phenolphthalein indicator. The crucible is heated for 1 hr. at 210°C. in an oven, converting the dipotassium phthalate alcoholate to dipotassium phthalate. The crucible is cooled in a desiccator for at least 1 hr., and weighed in the tared weighing bottle. The material weighed in the crucible consists of the dipotassium phthalate plus a small amount of  $K_2CO_3$  impurity. Correction for the impurity is made by dissolving the crucible contents in warm neutral distilled water, and titrating with 0.05 *N* HCl to the phenolphthalein end point. Milliliters of standard acid consumed times its normality times 0.1382 = grams  $K_2CO_3$ .

$$\text{Phthalate ester, per cent} = \frac{F \times P \times 100}{W}$$

where  $F$  = factor for converting dipotassium phthalate to the phthalate ester of the propellant,

$P$  = weight of dipotassium phthalate after correction for carbonate content, in grams,

$W$  = weight of sample in grams,

$F$  for dimethyl phthalate =  $\frac{0.801}{0.94} = 0.85$  (the factor being adjusted to compensate for a recovery of about 94% on synthetic samples of known dimethyl phthalate content),

$F$  for diethyl phthalate = 0.917,

$F$  for dibutyl phthalate = 1.148, and

$F$  for dioctyl phthalate = 1.610

**Procedure, Titrimetric**—The gravimetric procedure described above is followed through the stage where the precipitate of dipotassium phthalate alcoholate complex has been washed free from potassium hydroxide with absolute ether ethanol. The solvent wet precipitate is washed into a 250 ml Erlenmeyer flask with 30 ml of glacial acetic acid. Five drops of crystal violet indicator are added and the solution is titrated with standard perchloric acid in glacial acetic acid. The end point color change is from violet to blue. For buret reading temperature corrections (when sample titration is at a temperature different from that of the standardization) the factor 0.0011 ml per milliliter per degree centigrade is used.

$$\text{Phthalate ester, per cent} = \frac{V \times N \times M}{20W}$$

where  $V$  = standard perchloric acid solution in milliliters,

$N$  = normality of standard perchloric acid solution,

$M$  = molecular weight of the phthalate ester, and

$W$  = weight of sample taken for analysis in grams

#### POTASSIUM SALTS, AS SULFATE

See 'Sulfates by Gravimetric Methods' below p. 1400

#### POTASSIUM BY FLAME PHOTOMETER

See 'The Flame Photometer Procedure (Ca, Na, K)' p. 1376

#### POTASSIUM NITRATE BY NONAQUEOUS TITRATION

This titration method is applicable to propellants that may contain the following ingredients: nitrocellulose, nitroglycerin, diethyl phthalate, ethyl centralite and potassium nitrate, the latter in the range 0.5 to several per cent.

**Apparatus.** Titrimeter or pH Meter.—Equipped with glass and calomel electrodes.

**Buret System**—Buret with Teflon stopcock and a reservoir with the air inlet protected by a drying tube.

**Reagent.** Perchloric Acid, 0.02  $N$  Standard Solution in  $p$ -Dioxane or Glacial Acetic Acid.—Standardized against potassium acid phthalate (oven dried 1 hr

at 105°C.), dissolved in warm glacial acetic acid. Normality of the perchloric acid =  $\frac{\text{grams of potassium acid phthalate}}{0.2042 \times \text{milliliters of perchloric acid.}}$

**Procedure.**—Approximately 250 ml. of glacial acetic acid are transferred to a 300-ml., tall-form beaker, and brought to a vigorous boil on a hot plate. The beaker is removed from the hot plate, 5 g. of accurately weighed sample are added, and the beaker is returned to the hot plate. Boiling is continued for 15 min., adding more acetic acid if necessary, to keep the volume in the beaker at 150 ml. minimum. The beaker is then removed from the hot plate, and the contents are titrated immediately with 0.02 *N* perchloric acid, with agitation provided by a magnetic stirrer with a Teflon-coated bar.

$$\text{Potassium nitrate, per cent} = \frac{10.11NV}{W} \quad (\text{See Eq. 32-2.})$$

The electrodes are washed with acetone and dried before and after each titration. The calomel electrode is protected by a rubber membrane or by sleeve vent extrusion (depending on type of electrode used) against excessive entry of solvents and consequent contamination of the potassium chloride electrolyte.

#### POTASSIUM SULFATE BY NONAQUEOUS TITRATION

This titration method is applicable to propellants that may contain potassium sulfate in the range 0.5 to several per cent, and the following ingredients: nitrocellulose; nitroglycerin; dinitrotoluene; ethyl centralite; dibutyl phthalate; diphenylamine; lead stearate; carbon black; and graphite.

**Apparatus and Reagents.**—These are the same as those used above for determination of potassium nitrate.

**Procedure.**—An accurately weighed sample of the propellant, which will contain about 0.1 g. of potassium sulfate, is gradually transferred to a 500-ml., tall-form beaker containing 75 ml. of *chilled* morpholine (Hood).

**Caution.**—Morpholine is highly flammable; if finely divided propellant is rapidly added to warm morpholine, fire may result from the exothermic reaction.

The beaker is covered with a watch glass, and is placed on a steam bath if external heat is necessary to initiate reaction. When solvent action is complete, the liquid is decanted through a 12.5-cm. fine textured filter paper in a porcelain vacuum-filtration funnel, retaining in the beaker as much of the potassium sulfate (insolubles) as possible. The insolubles in the beaker and filter are rinsed with five 5-ml. portions of morpholine. Morpholine on the lip of the beaker or on outer surfaces is collected on a small piece of filter paper and added to the filter in the funnel. This filter is asperated to dryness, transferred to a glass funnel, and the apex is pierced. The beaker, after drying for about 20 min. at room temperature, is placed under the glass funnel, and the filter paper is washed with about 70 ml. of boiling hot distilled water. If a stirring rod was used it is rinsed with water and removed from the beaker. The beaker is heated on a hot plate until the solution is evaporated to dryness, care being taken to avoid spattering. Approximately 400 ml. of boiling glacial acetic acid are then added to the beaker and boiled for 30 min., the volume being maintained at a minimum of about 300 ml. by adding more hot acid when necessary. The beaker is removed from the hot plate, and the watch glass and sides of the beaker are washed down with acetic

acid The potassium sulfate is then titrated with 0.02 *N* perchloric acid *p* dioxane solution to a potentiometric end point

$$\text{Potassium sulfate, per cent} = \frac{17.426NV}{W} \quad (\text{See Eq. 32-2})$$

#### POTASSIUM SALTS BY THE TETRAPHENYLBORON METHOD<sup>35</sup>

**Reagents.** Aluminum Chloride, 0.2 *M* Solution (5 g. per 100 ml. Distilled Water)

Sodium Tetraphenylboron, 3% Solution—Nine g. of sodium tetraphenylboron are dissolved in 300 ml. of distilled water, 2 ml. of 0.2 *M* aluminum chloride are stirred in, and the solution is allowed to stand 30 min. It is then filtered into a polyethylene or Pyrex bottle.

Potassium Tetraphenylboron (Recrystallized from Acetone), Saturated Aqueous Solution

**Procedure.**—When barium salts are present in the propellant, the filtrate from the determination of barium as the sulfate is used for the potassium determination (see "Barium Nitrate or Other Barium Salts," p. 1375).

When lead salts are present in the propellant, the filtrate from the gravimetric determination of lead as the sulfate is used (see "The Sulfate Method," under Lead Compounds, p. 1389).

When neither lead nor barium is present the sample is digested with 65 to 70%  $\text{CH}_3\text{CO}_2\text{H}$ ,  $\text{HNO}_3$ , and  $\text{H}_2\text{SO}_4$  as described for the determination of lead as sulfate, repeating the nitric acid treatments until a colorless or nearly colorless solution is obtained when white fumes of sulfur trioxide appear.

In any case, the sulfate solution is evaporated to white fumes of sulfur trioxide and then heated until fuming ceases. An aliquot containing about 75 mg. of the potassium salts is suitable for their determination.

To the beaker containing the potassium salt 100 ml. of distilled water, 5 to 6 drops of 0.2 *M* aluminum chloride, and 3 to 4 ml. of concentrated  $\text{HCl}$  are added. The solution is cooled to 0° to 5°C. and then 20 ml. of 3% sodium tetraphenylboron solution (cooled to 0° to 5°C.) are added by pipet while the solution is stirred. The precipitate is allowed to settle for 5 min., and is then filtered by suction through a tared medium porosity, glass filtering crucible, maintaining slow continuous flow at all times during the filtration. The beaker and crucible are rinsed with four or five 20 ml. portions of a saturated aqueous solution of potassium tetraphenylboron at room temperature, and once with 10 ml. of cold distilled water (0° to 5°C.). The crucible is dried at  $120^\circ \pm 2^\circ\text{C}$  for 30 min., cooled in a desiccator, and weighed.

$$\text{Weight of precipitate} \times 0.2822 = \text{KNO}_3$$

$$\text{Weight of precipitate} \times 0.2432 = \text{K}_2\text{SO}_4$$

#### SODIUM BY FLAME PHOTOMETER

See "The Flame Photometer Procedure (Ca, Na, K)," p. 1376

#### SULFATES BY GRAVIMETRIC METHODS

Potassium sulfate is determined in some propellants by weighing as such, utilizing either the filtrate from the determination of lead as the sulfate or, in the

<sup>35</sup> Based partly on the findings of Spoerck, K., and Williams, A. F. *Analyst*, 80, 347, 1955.

absence of lead, a filtrate prepared by the same preliminary wet-ashing procedure that is used for the lead determination, p. 1389. The filtrate is evaporated first in a beaker and then in a tared platinum dish. The dish is ignited at full-red heat over a Meker burner for 30 sec. and then cooled to room temperature. The residue in the dish is transferred quantitatively to a beaker using a distilled water jet and a rubber policeman. The solution is filtered through a rapid filter paper, re-evaporated, and reignited in the platinum dish. The dish is cooled in a desiccator and weighed. The gain in weight above the tare weight of the platinum dish is taken as potassium sulfate from the sample taken for analysis.

Sulfates from some propellants are determined by the conventional gravimetric determination as  $\text{BaSO}_4$ , following extraction of the sample with hot water or hot dilute acid.

The presence of calcium carbonate (or other calcium salts) in a propellant creates difficulties in the sulfate determination. Several procedures have been proposed, but no simple method has been found suitable for standard usage.

#### TIN BY THE IODIMETRIC METHOD

**Reagents.** Iron Wire, No. 36 Gauge, 99.8% purity.

**Antimony Chloride Solution.**—Heat 3.5 g. of  $\text{Sb}_2\text{O}_3$  in 100 ml. of  $\text{HCl}$  to complete solution, and then dilute to 500 ml. with distilled water.

**Procedure.**—An accurately weighed sample of about 2 g. of propellant is placed in a 250-ml. Erlenmeyer flask (equipped with a side tube for introduction of inert gas) and heated on a steam bath with 10-ml. of glacial acetic acid, 10 ml. of  $\text{HNO}_3$ , and 5 ml. of  $\text{H}_2\text{SO}_4$  until solution is complete. Five ml. of  $\text{H}_2\text{SO}_4$  are added, and the flask is heated on a hot plate until dense white fumes of sulfur trioxide appear. More  $\text{HNO}_3$  is added drop by drop until all carbonaceous matter has decomposed. The flask is cooled to room temperature, and the sides are washed down with a fine jet of distilled water. The flask is reheated on the hot plate until sulfur trioxide fumes cease. The flask is again cooled, and 50 ml. of distilled water, 50 ml. of  $\text{HCl}$ , and 100 ml. of antimony chloride solution are added. A piece of iron wire, weighing about 0.5 g., is added to the flask, and the flask is heated until the iron has completely dissolved.

Inert gas ( $\text{CO}_2$  or  $\text{N}_2$ ) is passed through the inlet tube during the remainder of the determination. Twenty g. of metallic nickel are added to the flask, a 2-hole rubber stopper is inserted in the neck, and the flask is heated gently for 15 min. The flask is cooled in cold water. Five ml. of starch indicator solution are added, and the flask contents are titrated with 0.02 *N* iodine solution to the first permanent blue color.

$$\text{Tin (Sn), per cent} = \frac{5.935NV}{W} \quad (\text{See Eq. 32-2.})$$

#### TIN AND GRAPHITE BY GRAVIMETRIC METHOD

**Procedure.**—A 3- to 5-g. sample of propellant, in a 300-ml. tall-form beaker covered with a ribbed glass, is moistened with 5 to 10 ml. of water, and 40 to 50 ml. of 70%  $\text{HNO}_3$  are added. The beaker is gently heated until decomposition is complete, and then the solution is boiled until its volume is reduced to 10 ml. The cover glass and inner walls of the beaker are washed down with 5%  $\text{HNO}_3$ , and the solution is filtered through a tared Gooch crucible. The precipitate in

the crucible is thoroughly washed with warm distilled water, and the filtrate is discarded (Caution—Do not allow nitric acid and acetone to come together)

The precipitate is washed with acetone and then again with warm distilled water. The crucible is dried in an oven at 350°C for 40 min, is cooled in a desiccator and weighed.

The crucible is then ignited in a muffle furnace at 800°C for 1 hr, cooled, and reweighed.

$$\text{Tin (Sn), per cent} = \frac{78.77(C - A)}{W}$$

$$\text{Graphite, per cent} = \frac{100(B - C)}{W}$$

where  $A$  = tare weight of crucible in grams,

$B$  = weight of crucible and precipitate after drying at 350°C, in grams,

$C$  = weight of crucible and precipitate after ignition at 800°C, in grams, and

$W$  = weight of sample taken for analysis in grams

### TIN DIOXIDE BY VOLATILIZATION

**Procedure**—A 2 g sample of propellant is gently heated in a 250 ml Erlenmeyer flask with 30 ml of  $\text{HNO}_3$  until complete decomposition has taken place and the volume is reduced to 10 ml. The side walls of the flask are washed down with 20 ml of 5%  $\text{HNO}_3$  and the contents of the flask are filtered through a rapid quantitative filter paper. The paper and residue are washed with hot distilled water transferred to a porcelain crucible, and the paper is slowly charred by heating at about 315°C. The crucible is then ignited in a muffle furnace at 800° to 825°C, cooled, and weighed. It is reignited until constant weight (within 3 mg) is achieved. One half g of ammonium iodide is added to the crucible and mixed with the residue. The crucible is then ignited in a muffle furnace at 430° to 470°C until fuming has ceased (about 15 min). After cooling the volatilization with ammonium iodide is repeated. After cooling the crucible again, 3 ml of  $\text{HNO}_3$  are added and carefully evaporated to dryness on a hot plate. The crucible is then heated to constant weight in a muffle furnace at 800° to 825°C.

A blank is run on the ammonium iodide reagent by the volatilization procedure.

$$\text{Tin dioxide (SnO}_2\text{), per cent} = \frac{(A - V + B)100}{W}$$

where  $A$  = weight of crucible and residue ( $\text{SnO}_2$ ) just prior to volatilization with ammonium iodide, in grams,

$V$  = weight of crucible after volatilization, in grams,

$B$  = blank in grams, and

$W$  = weight of sample taken for analysis in grams

### TRIACETIN BY CHROMATOGRAPHIC ACID HYDROLYSIS METHOD<sup>23</sup>

This chromatographic acid hydrolysis procedure is applicable to double base propellants, and is suitable when any of the following ingredients, in addition to the triacetin, are present: nitrocellulose, nitroglycerin, dibutyl phthalate, dioctyl

<sup>23</sup> Based on the method described by Watts, J. D., and Stalcup, Harry, *Anal. Chem.*, **28**, 975, 1956.

phthalate; ethyl centralite; 2-nitrodiphenylamine; diphenylamine; and dinitrotoluene.

**Apparatus.** Chromatographic Tube.—The tube should be 35 mm. in diameter and at least 200 mm. long (or Size No. III chromatographic tube with fritted-glass disc sealed to inner joint connection).

**Suction-Filtration Apparatus.**

**Soxhlet Unit.**—An all glass unit with siphoning-cup capacity of 25 to 40 ml.

**Solvents.** Methylene Chloride, Redistilled (Fisher Reagent Grade).

Diethyl Ether, Anhydrous.—Redistilled from sodium hydroxide pellets.

Acetone, Analytical Reagent Grade.

Methanol, Technical Grade.

**Reagents and Solutions.** Solution A.—A solution containing 5% hydroxylamine hydrochloride in 10% potassium hydroxide is freshly prepared each week.

Solution B.—A solution containing 2% ferric chloride in 1.0 *N* hydrochloric acid is prepared as required.

**Adsorbent Test Solution.**—An adsorbent test solution is prepared by dissolving 0.20 g. of triacetin (reagent-grade) and 0.033 g. of 2-nitrodiphenylamine (reagent-grade) in 30 ml. of redistilled methylene chloride.

**Adsorbent.**—Two parts by weight of silicic acid, Baker or Mallinckrodt (9% water), are thoroughly mixed with 1 part of Celite (Johns-Manville Hyflo Super-Cel).

**Preparation of Adsorbent.**—A large quantity of the adsorbent is washed with solvents to remove any soluble material, then it is dried, heated, and stored ready for use. Used adsorbent should be washed in the same manner.

A 90 by 90 mm. fritted-glass, Büchner funnel, assembled to a suction-filtration apparatus, is prepared. With the suction applied from a water aspirator or other source of vacuum, the adsorbent is slowly added and packed until the funnel is filled to within 0.25 in. of the top. The surface of the adsorbent is then smoothed and packed with the flat end of a wooden rod prior to the addition of the solvents. With the suction still applied, the following solvents are added in the order listed, each new solvent being added just before the top of the column goes dry: 1-V diethyl ether; 1-V acetone; and 1-V methanol; V being defined as the minimum quantity of liquid required to wet the entire adsorbent.

The adsorbent is removed from the funnel and air-dried until practically all solvents are evaporated; it is then heated in an oven for 24 hr. at 150° to 160°C.

The adsorbent may be stored in 0.5-gal. Mason jars, containing a few pebbles from 0.5 to 1 in. in diameter, to facilitate complete breakdown of any lumps. The material is shaken vigorously to fluff it, and is transferred to another jar just prior to use in the column.

**Preparation and Adsorptive Test of Chromatographic Column.**—A chromatographic tube, about 35 mm. in diameter and between 200 and 250 mm. long, is assembled to a suction-filtration apparatus. If the tube is not provided with a coarse porous disc, a plug of glass wool is inserted into the bottom. The adsorbent is added to the tube until a column about 12 cm. high is formed. Suction from a vacuum line (vacuum of about 10 mm. of mercury) is then turned on, and the top of the column is leveled. If the column height goes below 10 cm., additional silicic acid is added until the column height is 10 cm. A porcelain porous disc is placed on top of the column. Suction is again applied, and the following solvents and solutions are added to the column in the order listed, each new solvent



hydrochloric and liberated acetic acids are titrated with standard 0.1 N NaOH, phenolphthalein being used as the indicator. A blank is run on 25 ml. of the standard acid in the same manner as the sample.

$$\text{Triacetin, per cent} = \frac{7.3N(V - B)}{W} \quad (\text{See Eq. 32-1.})$$

## COMPOSITE PROPELLANTS

Cured composite propellants are difficult to analyze because of the reactions (e.g., crosslinking) that take place during curing, and the unfavorable character of the finished product with respect to solubility in solvents. Most of the analyses published to date are applied to ingredients used in manufacturing the composite propellants or to uncured propellants rather than to the finished products. Physical tests (such as tensile strength) and thermodynamic tests (such as burning rate and heat of explosion) are relied upon more extensively in examining cured composite propellants than are chemical analyses at present. A number of the chemical methods that are in use are security-classified and cannot be included here.

### SAMPLE PREPARATION

Some composite propellants can be ground in a Wiley mill with safety; others cannot. In some cases, suitable specimens for analysis can be produced by feeding dry ice to a Wiley mill along with small pieces of propellant. Samples containing powdered metals should not be ground in a Wiley mill because of their tendency to produce specimens with partially segregated metallic components. Grinding in the Wiley mill may also cause undesirable separation of the oxidizer component, even though no added metallic constituents are present. Microtoming is often advantageous because of safety factors and the thin shavings that can be obtained. Suitable samples are at times prepared by cutting thin sheet stock with shears, and often strands prepared for the burning-rate test are found to be convenient and are made abundantly available.

### SOLVENT EXTRACTION

Extraction with water and with organic solvents is routinely applied to uncured composite propellants as the initial step in analysis after suitable comminution. For some types of cured propellant, inorganic nitrates or perchlorates may be satisfactorily extracted with water. The metallic component of some cured propellants is determinable gravimetrically after separation by standing for a considerable period of time with an organic solvent or by a refluxing operation. Acetone, chloroform, pyridine, butyl acetate, and dimethylformamide are typical of the solvents occasionally found suitable. In all the methods of analysis described here, which call for a water-extracted ammonium or potassium salt, it should be remembered that direct Soxhlet or Wiley extraction with water is applicable only to certain types of composite propellants. Methods for extracting propellants containing asphaltic or rubber binders have not been available. Liquid-liquid extraction methods may be found suitable in some cases.

### MOISTURE BY KARL FISCHER TITRATION

Oven drying and carbon tetrachloride distillation methods are used to a limited extent for moisture in composite propellants, but the Karl Fischer titration is generally considered preferable. The latter is applied to both cured and uncured

specimens as well as to the ingredients used in manufacturing the propellant (For details of the procedure see "Moisture by Karl Fischer Titration," above, p 1290)

### AMMONIUM NITRATE OR AMMONIUM PERCHLORATE BY KJELDAHL METHOD

Following extraction from the propellant with water, the ammonium nitrate or perchlorate is determined by the well known Kjeldahl distillation technique. The extract is usually concentrated by boiling after addition of a slight excess of  $H_2SO_4$ . It is then placed in the distillation flask, a few pieces of mossy zinc are added, an excess of NaOH solution is added and the liberated ammonia is distilled into a measured quantity of standard mineral acid solution or a saturated solution of boric acid. The excess standard acid is back titrated with standard alkali or, if the boric solution is used, the absorbed ammonia is titrated directly with standard acid. Methyl red is used as indicator in either case.

$$\text{Ammonium nitrate, per cent} = \frac{8.005NV}{W}$$

$$\text{Ammonium perchlorate, per cent} = \frac{11.75NV}{W} \quad (\text{See Eq. 32-2})$$

### AMMONIUM NITRATE OR AMMONIUM PERCHLORATE BY THE FORMALDEHYDE METHOD

**Procedure**—An accurately weighed sample of about 5 g. of propellant is extracted with distilled water in a Soxhlet or Wiley apparatus. The extract is made up to 250 ml. in a volumetric flask and 50 ml. of this solution are transferred to a 250-ml. beaker containing 50 ml. of 37 to 38% formaldehyde which has been neutralized by addition of 0.2 N sodium hydroxide solution. For the neutralization, 3 to 5 drops of phenolphthalein or thymolphthalein are used as indicator, or the solution is brought with the alkali to a pH of 8.5 using a pH meter and glass and calomel electrodes. The solution is titrated with 0.2 N NaOH solution to a phenolphthalein or potentiometric end point and then an excess of 2 ml. of the standard alkali is added. The beaker is covered and allowed to stand 45 min. The solution is back titrated with 0.05 N standard HCl to a very faint pink end point with phenolphthalein, or to pH 8.5 potentiometrically.

$$\text{Ammonium nitrate, per cent} = \frac{8.005(AN - BN')}{W}$$

$$\text{Ammonium perchlorate, per cent} = \frac{11.75(AN - BN')}{W} \quad (\text{See Eq. 32-4})$$

where  $W$  = grams of sample in aliquot

### AMMONIUM NITRATE BY NONAQUEOUS TITRATION

**Apparatus** Titrimeter or pH Meter.—Equipped with glass and calomel electrodes.

**Buret System**.—Buret with Teflon stopcock and a reservoir, with the air inlet protected by a drying tube.

**Reagents** Perchloric Acid, 0.1 N Standard Solution in Glacial Acetic Acid  
Sodium Acetate, 0.1 N Standard Solution in Glacial Acetic Acid

*Procedure.*—An accurately weighed sample of about 0.4 g. of propellant is digested in a 250-ml. beaker with 100 ml. of glacial acetic acid and 10 ml. of acetic anhydride for 30 min. with magnetic stirring. An excess of the standard 0.1 *N* perchloric acid solution (e.g., 50 ml.) is added, the solution is stirred for 2 min., and the excess acid is back-titrated with the standard 0.1 *N* sodium acetate solution to a potentiometric end point.

$$\text{Ammonium nitrate, per cent} = \frac{8.005(AN - BN')}{W} \quad (\text{See Eq. 32-4.})$$

#### AMMONIUM NITRATE BY FERROUS REDUCTION METHOD

*Procedure.*—An aliquot from an acetic acid extraction (reflux and filtration) or distilled water extraction (Soxhlet or Wiley apparatus) of a propellant is taken, which will contain 0.2 to 0.4 g. of ammonium nitrate. The aliquot is diluted in a special titration flask (see Fig. 32-14) to a volume of 50 ml. with distilled water. A stream of inert gas ( $\text{CO}_2$ ) is passed into the titration flask through the side arm at this stage, and is continued throughout the determination. Twenty-five hundredths g. of sodium chloride is added to the flask, and then 20.00 ml. of 0.4 *N* ferrous ammonium sulfate solution are added from a buret (protected by  $\text{CO}_2$ ). From a dispensing buret, 30 ml. of concentrated  $\text{H}_2\text{SO}_4$  are added with constant agitation by swirling. The flask is connected to a Graham reflux condenser, and the solution is brought to boiling on an electric hot plate and boiled for 5 to 10 min. The flask is cooled, the flask-condenser connection loosened slightly, and the condenser washed down by pouring 30 ml. of water into the top of the condenser. The flask contents are then titrated with 0.2000 *N* potassium dichromate solution using ferroin as indicator.

$$\text{Ammonium nitrate, per cent} = \frac{2.668N(B - A)}{W} \quad (\text{See Eq. 32-3.})$$

where  $W$  = grams of sample in aliquot.

#### MIXED OXIDIZERS, AMMONIUM NITRATE, AND AMMONIUM PERCHLORATE

Propellants containing both ammonium nitrate and ammonium perchlorate may be analyzed for each component separately, or one only of the components may be determined directly and total oxidizer content determined by the Kjeldahl or formaldehyde procedures. The ferrous reduction or the nonaqueous titration method is suitable for determining ammonium nitrate in the presence of the perchlorate, and the fusion-Volhard procedure is valid for determining the chlorate in presence of the nitrate.

## Appendix A

# PARTIAL LIST OF SPECIFICATIONS AND ABBREVIATIONS RELATED TO EXPLOSIVES, PROPELLANTS, OR THEIR INGREDIENTS

The military specifications listed below were consulted in the preparation of this chapter. The list also shows some of the abbreviations (other than chemical symbols) that are commonly applied to materials used in the explosives industry.

<i>Material</i>	<i>Abbreviation</i>	<i>Specification</i>
Aluminum	—	JAN-A 289, 512, 667
Ammonium nitrate	AN	JAN A-175
Ammonium perchlorate	AP	JAN-A-192
Ammonium picrate	—	JAN A 166A
Antimony sulfide	—	JAN-A-159A
Barium carbonate	—	JAN B 624
Barium chromate	—	JAN-B-550
Barium nitrate	—	Mil B 162B
Barium peroxide	—	JAN B 153
Barium stearate	—	JAN-B-366
Calcium oxalate	—	JAN C 628
Calcium stearate	CaSt	—
Carbon black	CB	JAN C 306
Cellulose acetate	CA	—
Cellulose nitrate ("nitrocellulose")	NC	JAN-N-244
Composition B	Comp B	JAN C 401
Copper (powdered)	—	JAN C 768
Cyclotetramethylenetetranitramine	HMX	—
Cyclotrimethylenetrinitramine	RDX	JAN-R 398
Diazodinitrophenol	DDNP	JAN-D-552
Dibutyl phthalate	DBP	JAN D 218
Diethyleneglycoldinitrate	DEGDN	—
Diethyl phthalate	DEP	JAN D-242
1,1-Dimethylhydrazine (unsymmetrical)	UDMH	Mil-D 25604B
Dimethyl phthalate	DMP	JAN-D 709
Dinitroethylenediamine (Haleite)	LDNA	—
Dinitroglycerin	DNG	—
Diminitoluenes	DN I	JAN D 204

<i>Material</i>	<i>Abbreviation</i>	<i>Specification</i>
Diocetyl phthalate (di-2-ethylhexyl phthalate)	DOP	Mil-D-13796
Diphenylamine	DPA	JAN-D-98
Ethyl centralite	EC	JAN-E-255
Ethyleneglycoldinitrate	EGDN	—
Ethylene oxide	—	Mil-P-8845 ASG
Glyceryl trinitrate (nitroglycerin)	NG	JAN-N-246
Graphite	—	JAN-G-155
Hexachlorethane	—	JAN-H-235
Hydrazine	—	Mil-H-26536
Hydrogen peroxide	—	Mil-H-16005C
Iron oxide, ferric	—	JAN-I-706
Iron oxide, magnetic	—	JAN-I-275
Lead azide	—	Mil-L-3055
Lead chromate	—	JAN-L-488
Lead dioxide (peroxide)	—	JAN-L-376
Lead stearate	PbSt	—
Lead styphnate	—	Mil-L-16335, 17186
Magnesium (powdered)	—	JAN-M-382A
Magnesium stearate	MgSt	JAN-M-542
Manganese (powdered)	—	JAN-M-476A
Mercury fulminate	—	JAN-M-219
Mononitrotoluene	MNT	—
Nickel (powdered)	—	JAN-N-412A
Nitric acid, fuming (red and white)	RFNA, WFNA	Mil-P-7254E
2-Nitrodiphenylamine	2NDPA	Mil-N-3399
Nitrogen dioxide (dinitrogen tetroxide)	—	Mil-P-26539-(USAF) tentative
Nitroguanidine	NO <sub>2</sub> G	JAN-N-494
Oxygen	—	Mil-P-25508
Pentaerythritol tetranitrate	PETN	Mil-P-387A
Pentaerythritol trinitrate	PETriN	—
Phosphorous, red	—	JAN-P-211
Phosphorous, red, stabilized	—	JAN-P-670
Picric acid (2,4,6-trinitrophenol)	—	JAN-A-187
Polypropylene glycol	PPG	—
Potassium chlorate	—	JAN-P-150
Potassium nitrate	—	JAN-P-156-A
Potassium perchlorate	—	JAN-P-217
n-Propyl nitrate	—	Mil-N-8722A (USAF)
Sodium nitrate	—	JAN-S-322
Sodium oxalate	—	JAN-S-210
Strontium peroxide	—	JAN-S-612
Sucrose octanitrate (nitrosugar)	SON	—
Sulfur	—	JAN-S-487
Tetranitrodiglycerin	TNDG	—
Tin (pulverized)	—	JAN-T-458
Toluene diisocyanate	TDI	—
Triacetin	TA	JAN-T-301

<i>Material</i>	<i>Abbreviation</i>	<i>Specification</i>
Trinitrophenylmethylnitramine( <b>tetryl</b> )	—	JAN-T-339
Trinitrotoluene	<b>TNT</b>	JAN-T-248
Zinc (dust)	—	JAN-Z-365
Zinc oxide	—	JAN-Z-291B
Zirconium (powdered)	—	JAN-Z-399A

## Chapter 33

# NATURAL FATS

By Virgil C. Mehlenbacher

Quality Assurance Department  
Swift and Co.  
Chicago, Ill.

### SAMPLING <sup>1</sup>

Bulk oil is best sampled if the product to be sampled is completely liquid and thoroughly mixed. In such cases, a core sample or even a sample dipped from the tank while the oil is undergoing vigorous agitation will be representative.

Settled material including water and solid impurities, when concentrated at the bottom of a tank, are difficult to reconstitute in proportional quantities. The contour of the tank must be taken into account. If the bottom of the tank is smaller than the middle, as in the case of a tank car, a simple core sample is not representative unless the contents are well mixed. To overcome this, the number of portions from each section (e.g., each 1-foot level) should be regulated in reverse order to the cubical capacity of each section. For example, if the bottom 1-foot section is one-fourth the capacity of the middle 1-foot section, then one 1-foot sectional sample should be drawn from the bottom level and four 1-foot sectional samples from the middle section. These portions are then composited into one sample and mixed.

### TANK CARS—LIQUID CONTENTS <sup>2</sup>

The sampler is a metal tube with a 2-inch diameter throughout. The length must be sufficient to take a cross-section through the entire depth of oil which is about ten feet for tank cars. One end of the trier is fitted with a tight valve which allows an unrestricted opening two inches in diameter when fully opened and free from leaks when closed. The valve is opened and closed by means of a rod from the top of the trier. The trier is so constructed as to take a sample within  $\frac{1}{4}$  in. (or less) of the bottom of the tank. Such a sampler suitable for tank cars may be obtained from the Refinery Supply Company, Tulsa, Oklahoma.

*Procedure.*—Lower the oil trier vertically through the oil at a uniform rate with the bottom valve completely open so that 10 to 15 seconds will be required to reach the bottom of the car. It is necessary that the trier be lowered slowly into the oil, so that the levels of oil inside and outside of the trier remain the same. Otherwise, an unduly large portion will be drawn from the bottom which is likely to contain a

<sup>1</sup> American Oil Chemists' Society, *Official and Tentative Methods*, 2nd ed., Chicago, 1946.

<sup>2</sup> Method of the National Cottonseed Products Association and the National Soybean Processors Association.

The  $\frac{3}{8}$  inch bleeder line is  $\frac{3}{8}$  inch standard pipe with a slight downward slope, located in a vertical section of the pumping line through which the product is continuously flowing upward to the individual tank or tank car being sampled. The sample line should be located as far away from elbows or tees as possible, should penetrate to the center of the pumping line, should be cut beveled at the end looking downward, and should discharge into a sample tank or drum as illustrated in the accompanying sketch. The sample line should not have a petcock.

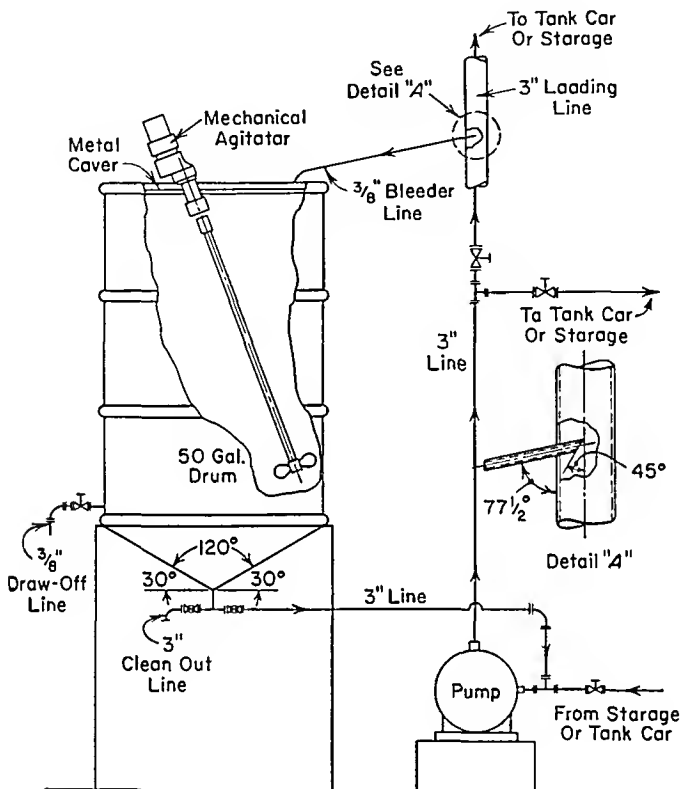


FIG. 33-1. Apparatus for Continuous Flow Sampling.

The metal sample tank or drum is of approximately 50-gallon capacity having a suitable metal cover, and an inverted cone bottom welded securely in place. Just above the bottom of the drum a  $\frac{3}{8}$  inch draw-off line equipped with petcock is installed, and is used for obtaining the required sample(s) from the gross sample. To facilitate complete draining and easy cleaning, the bottom of the drum should be replaced by a securely welded inverted cone bottom having an apex angle of approximately  $120^\circ$ , the other two angles with the horizontal being about  $30^\circ$  each. To prevent loss of solvent by evaporation, a suitable metal cover, with slots or holes to permit insertion of sampling pipe and mixer shaft, should be placed over the sample tank during the sampling and mixing operation.

Prior to the start of the pumping period, the sampling equipment should be examined and the draw-off line closed. During the pumping period it should be



TABLE 33-1. ADDITIONAL METHODS EMPLOYED FOR THE DETERMINATION OF WATER IN NATURAL FATS

<i>Method</i> <sup>1</sup>	<i>Sample (Grams)</i>	<i>Procedure</i>
Air Oven at 101°C.	5	Dry for 30-minute periods until loss does not exceed 0.05% in one period.
Vacuum Oven at 20–25°C. above boiling point of water at operating pressure	5	Dry for 60-minute periods until loss does not exceed 0.05% in one period.
Distillation	Depends on H <sub>2</sub> O content	Distil with toluene in Bidwell-Sterling apparatus. Measure water collected in receiver.

**HOT PLATE METHOD**

**Procedure.**<sup>1</sup>—Weigh 5 to 20 grams of well mixed sample into a dried and tared 150-ml. beaker. Place the beaker containing the sample on a hot plate and rotate the beaker gently to avoid spattering. The approach of the end point is judged by the cessation of rising bubbles of steam as well as by the absence of foam. The end point may also be determined by placing a clean watch glass over the beaker. Condensation on the watch glass due to the evolution of steam from the sample indicates that moisture is still present. Do not allow the temperature of the sample to exceed 130°C., but when the apparent end point has been reached heat the sample momentarily to the point of incipient smoking. Discontinue heating immediately at this point and cool and weigh the beaker and contents.

$$\% \text{ Moisture and volatile matter} = \frac{\text{Wt. of residue} \times 100}{\text{Wt. of sample.}}$$

**THE KARL FISCHER TITRIMETRIC METHOD**

**Reagents.** Solution *A*.—Add 180 g. of sulfur dioxide to 1800 ml. of a mixture of pyridine and methanol (1 + 1, v/v), previously cooled to about 4°C. Add the gas to the liquid through a glass tube arranged to discharge below the surface of the liquid. If the solution becomes hot, interrupt the flow of gas and cool the solution before proceeding. When sufficient gas has been added, stopper the flask with a rubber stopper fitted with a drying tube and adjust the contents to room temperature.

Solution *B*.—Dissolve 120 g. of iodine in anhydrous methanol and then make to a volume of two liters with anhydrous methanol.

Solutions *A* and *B* described above should be maintained in bottle and buret assemblies well protected with drying tubes to prevent the absorption of water from the atmosphere or from any other source. Also, it is advisable to minimize exposure to atmospheric moisture of the sample and any part of the apparatus coming in contact with the reagents or sample during the determination.

**Standardization of Solutions.**—Measure accurately from a buret 25.0 ml. of solution *A* into a clean dry flask. Insert a 1-hole stopper into the neck of flask and connect directly to the buret containing solution *B* with suitable connections so that the titration can be performed with a minimum of contact with the atmosphere. Titrate, stirring or shaking during the titration, to the appearance of a red color that persists for 10 seconds. Add solution *B* slowly (0.2-ml. increments) when approaching the end point. Add 0.05 g. of water using a weighing buret

## FREE FATTY ACIDS

The method described below for the determination of free fatty acid content is applied to animal and vegetable fats and oils.

TABLE 33-2.

<i>FFA Range</i>	<i>Grams of Sample</i>	<i>Ml. of Alcohol</i>	<i>N of Titrant</i>
0-0.2	56.4	50	0.1—NaOH
0.2-1.0	28.2	50	0.1—NaOH
1.0-30.0	7.05	75	0.25—NaOH
30.0-50.0	7.05	100	0.25 or 1.0—NaOH
50.0-100	3.525	100	1.0—NaOH

**Procedure.**<sup>1</sup>—Weigh the required quantity (see Table 33-2) of sample into a convenient flask or bottle and add the indicated amount of neutral 95% ethyl alcohol. Add 1 ml. of 1% phenolphthalein in 95% ethyl alcohol. Warm the mixture slightly and titrate with standard sodium hydroxide solution to the first pink color which persists for 30 seconds.

$$\% \text{ Free fatty acids as oleic} = \frac{\text{Titration} \times N \times 28.2}{\text{Wt. of sample}}.$$

To calculate free fatty acids in terms of lauric or palmitic acids insert the values 20.0 or 25.6 respectively in the place of 28.2 in the above equation.

Free fatty acid content is sometimes expressed as the acid value. This value is defined as the mg. of KOH equivalent to the acidity of one gram of sample. To calculate % free fatty acid (as oleic) to acid value, multiply the former by 1.99.

## UNSAPONIFIABLE MATTER

The unsaponifiable content of fats is usually defined as those substances which are soluble in the ordinary fat solvents, but which are not saponified by caustic alkalies. In normal fresh fats and oils these substances consist primarily of higher aliphatic alcohols, sterols, pigments and hydrocarbons.

The petroleum ether extraction procedure has been used for many years in connection with the analysis of animal and vegetable fats and oils, particularly in the United States. The ethyl ether method, in its present form, is more recent. Both methods yield comparable results on ordinary fats containing the usual amount of unsaponifiable content. However, the petroleum ether method is not satisfactory for fats containing high unsaponifiable content, such as the marine oils, and other fats which for one reason or another may contain more than the usual amount of unsaponifiable matter. In the latter cases the ethyl ether extraction method yields more nearly the correct results.

PETROLEUM ETHER EXTRACTION METHOD<sup>1</sup>

**Apparatus.**—Glass-stoppered extraction cylinder graduated at 40, 80 and 130 ml., height about 300 mm., diameter about 35 mm., capacity at least 150 ml.

**Procedure.**—Weigh accurately about 5 g. of well mixed sample into a 100- or 200-ml. Erlenmeyer or Soxhlet flask. Add 30 ml. of 95% alcohol and five ml. of aqueous potassium hydroxide (50% w/w). Boil gently but steadily under a reflux condenser for one hour or until the fat is completely saponified.

to separate completely and draw off the lower aqueous layer. Wash the ether twice more with 20-ml. portions of water, shaking vigorously each time and discarding the lower aqueous layers.

Wash the ethyl ether solution three times with 20-ml. portions of about 0.5 *N* aqueous potassium hydroxide solution, shaking vigorously each time. Wash after each alkali treatment with 20 ml. of water. If an emulsion forms during this washing procedure, allow as much separation as possible, discard the clear aqueous layer, and proceed to the next step, leaving any emulsion in the separatory funnel with the ether layer. After the third washing with 0.5 *N* potassium hydroxide, wash the ether with successive 20-ml. portions of water until the washings are no longer alkaline to phenolphthalein.

Transfer the ether solution to a 250-ml. beaker, rinsing the separatory funnel and its pouring edge with ether and adding the rinsings to the beaker. Evaporate to about 5 ml. and transfer quantitatively, with the aid of several small portions of ether, to a 50-ml. Erlenmeyer or Soxhlet flask which has been previously dried and weighed. Place the flask on a steam bath to remove the ether. When practically all of the ether has evaporated, add 2 or 3 ml. of acetone and remove all solvent completely by passing a gentle current of clean dry air through the warmed flask. Complete the drying to constant weight, preferably in a vacuum oven at 75° to 80°C. with an internal pressure of not more than 200 mm. of mercury. Cool in a desiccator and weigh.

After weighing, dissolve the contents of the flask in 2 ml. of ethyl ether and then add 10 ml. of 95% alcohol, previously neutralized to a faint pink color, using phenolphthalein indicator. Titrate with 0.02 *N* sodium hydroxide solution to the same final color. Correct the weight of the residue for free fatty acid content (1 ml. of 0.02 *N* NaOH is equivalent to 0.0056 g. of oleic acid). Also correct the weight of the residue for reagent blank obtained by conducting the determination in the same manner but omitting the sample.

#### Calculation.

$$\% \text{ Unsaponifiable matter} = \frac{(\text{wt. of residue} - \text{wt. of fatty acid} - \text{wt. of blank}) \times 100}{\text{Wt. of sample}}$$

#### ASH CONTENT<sup>1</sup>

(This method should not be applied to bodied oils containing lead or zinc.)

**Procedure.**—Weigh accurately about 50 g. of the sample into a 100-ml. platinum dish. Apply heat gently until the fat can be ignited by application of a small flame to the surface. Continue applying just enough heat to keep the sample burning.

When sufficient fat has been consumed to allow the addition of more, remove the heat source and allow the fat to cool until burning ceases. Then add another weighed portion and continue heating as before. Continue in this manner until a total of about 75 g. have been used. Continue heating until the residue assumes the appearance of a black charred mass and then heat in a muffle furnace at 550°–650°C. for one hour.

Cool and weigh the residue and repeat heating, cooling and weighing until the weight is constant.

$$\% \text{ Ash} = \frac{\text{Wt. of residue} \times 100}{\text{Wt. of sample}}$$

METALS<sup>5</sup>

Contamination by metals of vegetable and animal oils and fats usually results from contact with equipment or from some other processing or handling operation. Except where added for a specific purpose as, for example, metallic driers, many metals exert an undesirable influence on the quality of glyceride oils. Some metals, notably copper, are especially deleterious.

The metals most commonly found in fats and oils are usually present in small amounts such as a few parts per million so that the ordinary gravimetric and titrimetric methods are unsatisfactory for their quantitative estimation. The most useful techniques for this purpose are those based on colorimetry, polarography and spectroscopy. Colorimetric methods are presented here for the determination of nickel, iron and copper since these are probably the metals most commonly determined.

## NICKEL

**Procedure.**—Weigh 1, 10, or 50 g of sample into a 100 ml Vycor dish, depending upon the nickel content, as follows. For less than 2 p p m of nickel weigh 50 g, for 2–10 p p m of nickel weigh 10 g, and for 10–100 p p m weigh one g. Prepare the ash in a manner similar to that previously described but in this case the ashing temperature should not exceed 500°C and the time may be extended if necessary.

Add 1 ml of concentrated hydrochloric acid to dissolve the ash. Add more acid if necessary to dissolve the residue but keep the amount of acid at a minimum. Evaporate the solution almost to dryness at 160°C. Do not allow the solution to evaporate completely because this will result in volatilization of the nickel chloride and hence yield low results.

Dissolve the residue in distilled water and wash into a 50 ml glass stoppered volumetric flask. The total volume must not exceed 15 ml. Add to the flask 3 ml of saturated bromine water and allow to stand 1 minute. Add ammonium hydroxide (sp gr 0.90) a drop at a time until the excess bromine is destroyed as indicated by the disappearance of the brown color. Then add 5 ml of ammonium hydroxide.

If iron is present in excess of 2 p p m (as Fe) the solution must be filtered at this point. Dissolve the precipitate on the filter paper with a minimum of hydrochloric acid (1 + 1 v/v), wash the filter paper with distilled water, and collect the filtrate and washings in a beaker. Reprecipitate the iron with sufficient ammonium hydroxide (sp gr 0.90) to make the solution definitely alkaline but avoid a large excess. Refilter and wash the precipitate with distilled water, combine the filtrates and washings, evaporate to a volume of a few ml and transfer to a 50 ml volumetric flask. Proceed from here in the regular manner.

Add 10 ml of dimethylglyoxime solution (0.1 g in 100 ml of 95% alcohol) followed by 15–20 ml of 95% ethyl alcohol. Mix thoroughly, make up to volume with distilled water and again mix thoroughly. The reactions and color development must be carried out in diffused light, avoiding bright light or direct sunlight.

Allow the solution to stand 5 minutes to permit the full development of color and then immediately transfer a portion to a spectrophotometer cuvet and measure the transmittance at 445 mμ after adjusting the spectrophotometer to read 100% transmittance with an identical cuvet containing distilled water. Pre-

<sup>5</sup> Mehlenbacher, A. C., *The Analysis of Fats and Oils*, Garrard Press, Champaign, Ill. 1960.

pare and conduct a blank determination simultaneously and similar in all respects. The transmittance of the blank should be  $98 \pm 1\%$ . Determine the nickel content of the sample by reference to a concentration-transmittance graph prepared as follows:

**Preparation of Concentration-Transmittance Graph.**—Prepare a nickel solution of known concentration by dissolving 2.2617 g. of nickel sulfate ( $99\% \text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ ) in distilled water in a 500-ml. volumetric flask. Add 30 ml. of concentrated hydrochloric acid and bring to volume. This solution contains 1000  $\mu\text{g}$ . of nickel per ml. Make appropriate dilutions of this solution and process these as directed for the determination of nickel. The dilutions selected for development of the graph should contain such quantities of nickel as to cover the range of 0 to 100  $\mu\text{g}$ . Finally, plot a curve relating transmittance to micrograms of nickel.

$$\text{Nickel in p. p. m.} = \frac{(S - B)}{\text{Grams of sample}}$$

where  $S$  = micrograms of nickel in sample, and

$B$  = micrograms of nickel in blank.

#### IRON <sup>6</sup>

**Procedure.**—Prepare a hydroquinone solution containing 2.5 g. of hydroquinone and 1 ml. of hydrochloric acid (1 + 1, v/v) diluted to 100 ml. with distilled water.

Ash, as previously directed, a sufficient quantity of sample to provide 5–50 micrograms of iron. Add five ml. of hydrochloric acid (1 + 1, v/v) to the ash, cover the dish with a watch glass, and heat the contents just to boiling. Transfer the sample to a 50-ml. volumetric flask using distilled water to wash the last traces from the dish into the flask. Dilute to the 50-ml. mark with distilled water, mix thoroughly, and pipet 10 ml. into a cuvet. If the iron content of this portion is outside the limits of the concentration-transmittance graph, take a smaller aliquot and dilute to 10 ml.

Add 2 ml. of hydroquinone solution, 5 ml. of 1,10-phenanthroline solution (0.1% in distilled water), and 5 ml. of aqueous sodium acetate solution (20% w/v). These reagents should be added with a volumetric pipet and the solution thoroughly mixed after adding each reagent.

Conduct a blank determination along with the sample to make certain that none of the reagents is contaminated, and also to use as a reference solution against which the transmittance of the sample is measured. The transmittance of the blank is usually about 2% less than that of distilled water. If it is as much as 5% less than distilled water, new reagents should be prepared. The transmittance of the sample solution is measured in a spectrophotometer at 503  $m\mu$  with the instrument adjusted to read 100 per cent transmittance for the blank. Determine the iron content of the solution by reference to a concentration-transmittance graph prepared as follows:

**Preparation of Concentration-Transmittance Graph.**—Dissolve 0.1000 g. of pure iron wire in 10 ml. of 10% sulfuric acid and three ml. nitric acid (sp. gr. 1.43) and dilute to 1 liter with distilled water in a volumetric flask. Pipet 100 ml. of the standard iron solution into a 1-liter volumetric flask and dilute to volume with hydrochloric acid (1 + 19, v/v).

<sup>6</sup> Pohle, W. D., Cook, J. H., and Mehlenbacher, V. C., Food Research, 12, 229, 1947.

Pipet 0.5 1.0 2.0 3.0 4.0 and 5.0 ml of diluted standard iron solution into a series of cuvetts. Make up to 10 ml with dilute hydrochloric acid solution (1 + 19). Follow the procedure described above for developing the color and measuring the transmittance beginning with the addition of two ml of hydroquinone. Construct a concentration transmittance graph on semi logarithmic paper relating transmittance to micrograms of iron.

$$\text{Iron in p.p.m.} = \frac{\text{micrograms of iron in portion analyzed}}{\text{Grams of sample in portion analyzed}}$$

### COPPER

**Reagent**—Prepare a solution of 125 g of ammonium citrate in 500 ml of distilled water and add to this 100 ml of ammonium hydroxide (sp. gr. 0.90).

**Procedure**—Ash 5 g of sample as previously directed and add 40 ml of 0.1 N hydrochloric acid solution. If the residue does not dissolve, cover the dish with a watch glass, heat the mixture just to boiling, and then cool it to room temperature. Transfer the solution to a 125 ml separatory funnel and rinse the dish twice with 10 ml portions of 0.1 N hydrochloric acid, adding the washings to the separatory funnel. Add 15 ml of the ammonium citrate-ammonium hydroxide solution to the separatory funnel, mix thoroughly, and then add five ml of 0.05% aqueous sodium diethyldithiocarbamate solution and mix again. Add 15 ml of carbon tetrachloride with a pipet and shake vigorously to obtain complete extraction of the colored compound. Allow the solution to stand until the carbon tetrachloride layer separates. Filter the carbon tetrachloride portion through filter paper and measure the transmittance in a spectrophotometer at 430 mμ with the transmittance of the instrument previously adjusted to read 100% with carbon tetrachloride.

Prepare and conduct a blank determination using 60 ml of 0.1 N hydrochloric acid. Proceed otherwise as described for the sample, beginning with the addition of the ammonium citrate-ammonium hydroxide solution.

Prepare a graph relating transmittance to copper content from the analysis of samples of copper sulfate ( $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ ) solutions of known concentration. The dilutions selected for development of color should cover an appropriate range in μg of copper. Refer to the graph to determine the copper in the blank and in the sample and then calculate the copper content of the sample as follows:

$$\text{Copper in p.p.m.} = \frac{(S - B)}{\text{Grams of sample}}$$

where  $S$  = micrograms of copper in sample, and

$B$  = micrograms of copper in blank

### SOAP (Dissolved)

Sodium soaps may be present in oils which have been treated with sodium hydroxide or sodium carbonate as in the alkali refining process. Traces of soaps are difficult to remove in processing and they are not easy to determine analytically. Soap has been determined for many years by simply ashing the sample and then weighing or titrating the residue with standard acid. This method is satisfactory for determining soap content of some significant quantity but it is not satisfactory

for trace amounts. A titrimetric method has been used for small quantities with apparent success.

A method recently adopted by the American Oil Chemists' Society is based on comparison of the conductivity of a water extract of the sample with the conductivity of aqueous solutions of known concentrations of sodium oleate.<sup>7</sup>

#### ASHING METHOD

**Procedure.**—Incinerate 75–100 g. of sample following the procedure previously described for the determination of ash. Add 50 ml. of cold, boiled distilled water to the ash and titrate the solution with 0.02 *N* acid using methyl orange as the indicator.

$$\% \text{ Soap as sodium oleate} = \frac{\text{ml. 0.02 } N \text{ acid} \times 0.608}{\text{Wt. of sample}}$$

#### TITRIMETRIC METHOD

**Procedure.**<sup>8</sup>—Prepare a solution of acetone containing 2% of water, and, another solution of 0.1% bromophenol blue in 95% alcohol. Mix 0.5 ml. of the indicator solution with 100 ml. of the acetone-water solution and then add 0.01 *N* hydrochloric acid to the first appearance of a permanent yellow color.

Place 40 g. of sample in a test tube of convenient size and add to this one ml. of water. Warm the mixture and shake it vigorously. Add 50 ml. of the neutralized acetone to the soap solution, warm and shake again and then allow the mixture to stand until the layers separate. The presence of soap is indicated by a green or blue color in the upper layer.

Titrate with 0.01 *N* hydrochloric acid to the reappearance of the yellow color. Continue the process of warming, shaking and titrating until the yellow color of the upper layer remains permanent.

$$\% \text{ Soap as sodium oleate} = \frac{\text{ml. 0.01 } N \text{ acid} \times 0.304}{\text{Wt. of sample}}$$

This method is reported to be satisfactory for determining soap in oil within the range of 10–500 parts per million. The size of sample may be decreased for relatively high levels.

#### PHOSPHORUS

**Reagent.** Sodium Molybdate.—Carefully add 140 ml. of sulfuric acid (sp. gr. 1.84) to 300 ml. of distilled water. Cool to room temperature and add 12.5 g. of sodium molybdate. Dilute to 500 ml. with distilled water, mix thoroughly, and allow the solution to stand for at least 24 hours before use.

**Procedure.**<sup>1</sup>—Weigh 3.0–3.2 g. of sample and 0.5 g. of zinc oxide into a Vycor crucible. Heat the mixture on a hot plate until the mass thickens, then increase the rate of heating slowly until the mass is completely charred. Place the crucible in a muffle furnace and maintain at 550°–600°C. for two hours. Remove the crucible from the furnace and allow to cool to room temperature. Add five ml. of distilled water and five ml. of hydrochloric acid (sp. gr. 1.19) to the residue. Cover the crucible with a watch glass and heat at gentle boiling for 5 minutes.

<sup>7</sup> Goff Jr., H., and Blachly, F. E., *J. Am. Oil Chemists' Soc.*, **34**, 320, 1957.

<sup>8</sup> Wolff, J. P., *Oleagineux*, **3**, 197, 1948.

*Procedure.*<sup>9</sup>—Remove moisture and insoluble matter by filtering the sample before determining the neutral oil. Add 25 ml. of the solvent (methanol and absolute ethyl ether, (25 + 975), v/v) to the appropriate size of sample depending upon the approximate neutral oil content.

Neutral Oil Content %	Weight of Sample (g. $\pm$ 0.001 g.)
100-90	2-3
90-75	1-2
75-50	0.7-1
50-0	0.45-0.55

Attach a short piece of rubber tubing to the bottom end of a chromatographic column (20-mm. diameter, 400-mm. length, with sealed in coarse-porosity fritted disc). Close the outlet with a pinch clamp and fill the column about  $\frac{1}{3}$  full with the solvent. Add 19-21 g. of dry activated aluminum oxide (grade F-20 or equivalent) and wash down any oxide that may adhere to the sides of the column with a little solvent.

When ready to add the sample solution to the column, drain the solvent from the column until the upper level of the liquid is about 5 mm. above the upper surface of the aluminum oxide. Pour the sample and solvent into the column carefully so as not to disturb the surface of the oxide using four washings of about 6 ml. each of solvent to complete the transfer to the columns. Collect the eluate in a dried and tared beaker of convenient size. When the liquid level in the column drains to about 5 mm. above the surface of the alumina add 100 ml. of the solvent and then allow all of the solvent to pass through a column.

Wash the outlet of the column with a small amount of solvent and then evaporate all of the solvent on a water bath under a gentle stream of clean dry air. Continue drying for one hour in an oven at 105°C. Cool the beaker and contents and weigh.

$$\% \text{ Neutral oil} = \frac{\text{weight of residue} \times 100}{\text{Wt. of sample}}$$

### BREAK TEST

The *break test* is intended to provide a measure of the non-oil constituents of soybean oil. At best it is an inexact measure, and it is used primarily because of the absence of a more reliable method.

*Procedure.*<sup>1</sup>—Heat the sample to 75°C. and maintain at this temperature long enough to melt all fat-soluble particles.

Weigh 25 g. into a 180-ml. electrolytic type beaker, add three drops of hydrochloric acid (sp. gr. 1.19) and stir thoroughly. Suspend a thermometer ( $-6^{\circ}$  to  $400^{\circ}\text{C}$ ., AOCS specification H 5-40) in the center of the oil-acid mixture so that the bulb is completely immersed but not touching the bottom of the beaker. Apply heat so that the temperature rise will be  $75^{\circ}$  to  $80^{\circ}\text{C}$ . per minute.

Do not stir or otherwise disturb the sample after heating has begun. Heat to  $289^{\circ}\text{C}$ . and withdraw the flame. Cool to about  $25^{\circ}\text{C}$ . either in a water bath or in air.

After cooling and while stirring add 50 ml. of carbon tetrachloride to dissolve

<sup>9</sup> Tierney, S. E., J. Am. Oil Chemists' Soc., **34**, 348, 1957.



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TABLE 33-3. METHODS EMPLOYED FOR DETERMINATION OF STABILITY

<i>Method</i>	<i>Procedure</i>	<i>Reference</i>
Oxygen Absorption	Fat dispersed on sand, heated in special glass apparatus under atmospheric oxygen until pressure in flask is reduced to a specified amount.	E. W. Eckey, Oil and Soap, 23, 38, 1946.
Oxygen Absorption (ASTM Oxygen Bomb)	Fat dispersed on paper and heated in ASTM Oxygen Bomb under oxygen pressure until rate of absorption changes.	W. M. Gearhart, B. N. Stuckey and J. J. Austin, J. Am. Oil. Chemists' Soc. 34, 427, 1957.
Schaal Test	Sample in beaker is maintained at elevated temperature until odor becomes rancid.	V. C. Mehlenbacher, The Analysis of Fats and Oils, Garrard Press, 1960, p. 195.
Thiobarbituric Acid Test	Sample is treated with TBA reagent. Intensity of color related to fat condition.	ibid. p. 208.
Kreis Test	Sample is treated with phloroglucinol reagent. Intensity of color related to fat condition.	ibid. p. 191.

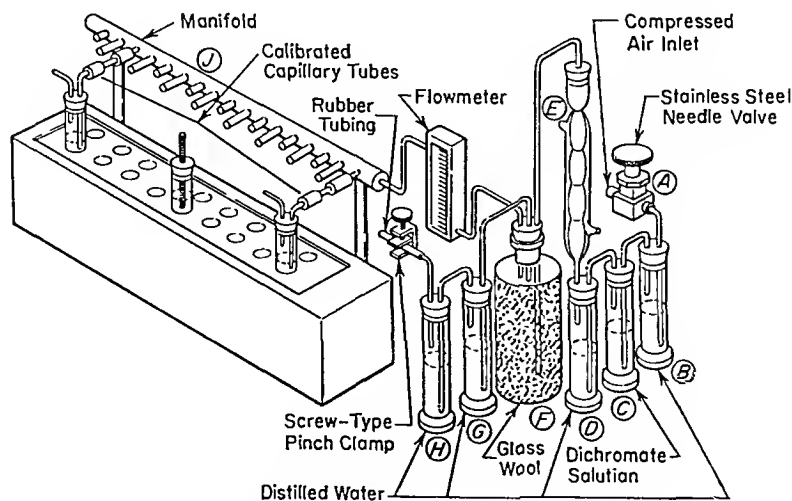


FIG. 33-2. Fat Stability Apparatus for Active Oxygen Method.

**Air Distributing Manifold** constructed of stainless steel nickel aluminum or glass. The glass capillary tubes must be calibrated to permit the same flow ( $\pm 10\%$ ) through each outlet when the total flow is adjusted to 2.33 ml per tube per second. Calibrated capillary tubes are available from certain laboratory supply houses.

**Air Purification Train**—*A* Air inlet tube from compressed air source equipped with stainless steel needle valve.

*B* Air washing column consisting of hydrometer cylinder 50 mm O.D. 375 mm high containing distilled water.

*C* Air washing column consisting of hydrometer cylinder 50 mm O.D. 375 mm high containing 2%  $\text{K}_2\text{Cr}_2\text{O}_7$  in 1%  $\text{H}_2\text{SO}_4$ . Fill to about 25 cm depth and replace solution after 72 hours of continuous operation.

*D* Air washing column consisting of hydrometer cylinder 50 mm O.D. 375 mm high containing distilled water. Fill to about 25 cm depth. Replace with fresh distilled water at the first appearance of a yellow color.

*E* Water cooled condenser Allihn 5 bulb type 300 mm jacket.

*F* Trap wide mouth 16 oz bottle containing glass wool.

*G* & *H* Pressure regulating columns hydrometer cylinders 50 mm O.D. 375 mm high containing distilled water. Fill to about 20 cm depth. Pressure regulation may also be obtained through the use of a suitable pressure regulating valve.

*J* Manifold.

**A Source of Clean Compressed Air**

**Sampling.** Due to peculiarities inherent in this procedure special precautions are necessary in obtaining and transporting samples. When packaged fats are involved the sample should consist of an unopened package if possible. Where this is impractical samples must be removed from large containers or processing equipment with clean sampling devices of stainless steel aluminum nickel or glass. Samples of solid fat should be taken at least 2 inches from the walls of large containers and 1 inch from the wall of small containers. If liquid oil is poured from a container the pouring spout or lip should first be thoroughly cleaned using a clean cloth moistened with acetone.

After removal from package or processing equipment samples should be transported or stored only in glass containers cleaned as herein described or in new tin containers. Under no circumstances should sample containers have plastic or enameled tops or covers with paper or waxed liners. Samples should be protected from contact with heat and air as much as possible.

**Cleaning Sample Containers and Aeration Assemblies.**—Melt and drain off as much of the fat from the previous determination as possible. Wash off the remaining fat with a suitable solvent. Petroleum ether is satisfactory if the cleaning is done immediately after the preceding determination and the fat involved is of 100 iodine value or less; otherwise acetone must be used.

Prepare a 1% solution of detergent (select type leaving no residue on glassware) and heat almost to boiling in the cleaning bath. Rinse out each test tube with the hot detergent solution brushing briefly with a nylon brush. Then place the tubes in a hot detergent solution in such a manner that the tubes are full and completely covered and so that no air bubbles are trapped within. Also immerse the fat free aeration tubes and stoppers in hot detergent solution so that they are completely covered and that no air bubbles are trapped within. Boil the solutions vigorously for 30 minutes. Brush each test tube vigorously with a nylon brush rinsing twice in the hot detergent solution. Rinse thoroughly with tap water followed by distilled water and place upright in a test tube rack. Fill with distilled

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water and allow to stand at least one hour. Rinse the aeration tubes thoroughly in tap water followed by distilled water and place upright in a clean two-liter beaker of distilled water in such a manner that the long straight tube and the stopper are covered. Allow to stand for at least one hour. At the end of this period, rinse both test tubes and aeration tube once again with fresh distilled water, drain on clean filter paper, and dry in an oven at 100°–105°C. Arrange washing and rinsing schedules so that test tubes and aeration tubes are dried at the same time. Assemble as soon as dry and store in a dust-free location.

**Procedure.**<sup>12</sup>—The control of temperature during heating and aeration of the sample, maintenance of absolute cleanliness, and elimination of contamination throughout the procedure cannot be overemphasized. The temperature refers specifically to the temperature of the sample in the tubes and not to that of the bath. If these factors are not rigidly observed, the results are likely to be incorrect. The nature of the AOM procedure is such that when errors occur, results tend to be below rather than above the true value.

Pour 20 ml. of oil or melted fat into each of two test tubes (25 × 200 mm.) which, for convenience, may be calibrated at the 20-ml. level. Place one of the tubes in the bath which has previously been brought to the desired temperature, insert the aeration assembly and connect it to the air-flow system, see Fig. 33-3. Stopper the second tube and keep at a cool temperature until it is to be heated. Start the second tube with the following spacing between tubes:

<i>Keeping Time</i>	<i>Spacing of Tubes</i>
0–16 hours	1 hour apart
16–32 hours	2 hours apart
32–50 hours	3 hours apart
Over 50 hours	4 hours apart

Maintain the contents of the tubes at the specified temperature and inspect the tubes regularly to be sure that the air is flowing properly. Heating and aeration is continued until a peroxide value is attained which corresponds to the point of inception of rancidity for the type of fat being tested. According to the standard method this is 100 meq./kg. of fat. It has been, however, common practice to use an end point of 20 meq./kg. for unhydrogenated animal fat and values of 75 to 125 for other oils and hydrogenated fats. It is desirable to continue heating without interruption to the end point, but if this cannot be done, the tubes should be chilled immediately on removal from the bath and kept chilled until ready to start the heating again.

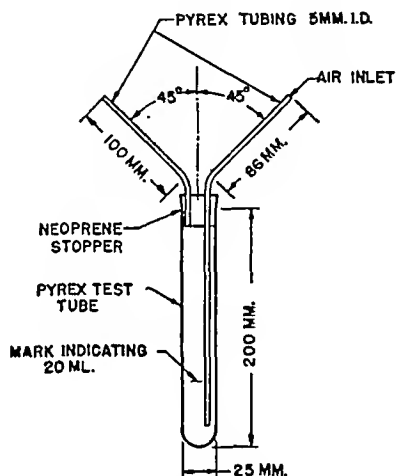


FIG. 33-3. Aeration Assembly for Active Oxygen Method.

When the end point is reached, determine the peroxide value of the sample and report the stability as the hours (to the nearest hour) required to reach the specified peroxide value. It is desirable that the leading tube should be beyond the specified peroxide level and the other tube slightly below this level, so that a reliable interpolation can be made. With a little practice, the odor of the air from the exhaust tube will be found to serve as a good indicator of the end point but because of the large personal variation in organoleptic sensitivity, odor cannot be accepted as the final criterion.

It is convenient, with long keeping samples to run a 'pilot tube' 12-15 hours in advance of the two test portions to obtain an approximation of the keeping time. Successive small samples (1 g) may be withdrawn from this tube to test for peroxide value as the rancid point is approached but this should be discontinued after a total of five grams have been removed. The pilot tube serves a twofold purpose. It enables the operator to continue the heating and aeration overnight with safety and it eliminates most of the guesswork from choosing the time for determining the peroxide content of the fat.

The AOM determination can and is now often run at 110°C instead of 97.8°C. In this case AOM hours at 97.8°C = AOM hours at 110°C  $\times$  2.5. Results are always reported in terms of the 97.8°C rate.

### PEROXIDE VALUE

**Procedure** <sup>1</sup>—Weigh  $5.00 \pm 0.05$  g of the sample into a 250 ml Erlenmeyer flask and then add 30 ml of the acetic acid chloroform solution (3 + 2, v/v). Swirl the flask until the sample is dissolved and add 0.5 ml of saturated potassium iodide preferably using a measuring type pipet. Allow the solution to stand with occasional shaking for exactly one minute and then add 30 ml of distilled water.

Titrate the mixture with 0.1 N sodium thiosulfate adding it gradually and with constant and vigorous shaking. Continue the titration until the yellow color has almost disappeared. Add 0.5 ml of starch indicator (1% in distilled water) and continue the titration. Shake vigorously near the end point to liberate all the iodine from the chloroform layer and add the thiosulfate solution dropwise until the blue color has just disappeared. If the titration requires less than 0.5 ml repeat the determination using 0.01 N sodium thiosulfate solution.

Conduct a blank determination on the reagents daily. The blank titration must not exceed 0.1 ml of the 0.1 N sodium thiosulfate solution.

$$\text{The peroxide value (meq/kg of fat)} = \frac{\text{Titration} \times N \times 1000}{\text{Wt. of sample}}$$

where  $N$  = normality of sodium thiosulfate

### IDENTIFICATION <sup>5</sup>

The identification of individual fats or oils is based on certain specific tests on the fatty acid composition and/or the physical and chemical characteristics. Identification of crude and refined oils can often be accomplished by determining the fat constants such as saponification value, iodine value, titer point, etc., and then comparing the results obtained with values of oils of known purity. However, there is considerable overlapping of values for known samples so that this comparison alone does not always provide positive identification. The fatty acid com-

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position and the presence of certain minor constituents will frequently serve to classify most of the common fats and oils, but some of these may be altered to some degree by processing. The so-called specific tests also are for the most part limited to unprocessed materials. It is obvious then that the problem of identification may not be a simple one. Processing and mixing may yield materials that almost defy the identification of the individual constituent oils.

Some of the identifiable characteristics of certain fats and oils are given in Table 33-4 and some of the more common methods follow. In Table 33-5 are given typical values for certain physical constants.

TABLE 33-4. SOME IDENTIFIABLE CHARACTERISTICS OF NATURAL FATS AND OILS

<i>Oil or Fat</i>	<i>Specific Characteristics</i>
Cottonseed and kapok oils	Halphen test
Sesame oil	Villavecchia test
Peanut oil	Bellier test
Teaseed oil	Modified Liebermann-Burchard test
Kapok oil	Besson test
Coconut and Babassu oils	High saponification value, contain lauric acid
Marine oils	High squalene content, insoluble bromide test
Vegetable butters	Crystallization tests
Tung and oiticica oils	Contain conjugated fatty acids
Butter fat (milk fats)	Contain butyric and other low molecular weight fatty acids
Animal fats	Contain cholesterol
Beef fats and hydrogenated vegetable oils in lard	Bömer value
Vegetable oils in animal fats	Detection of high melting sterols
Olive oil	Contains squalene
Castor oil	Solubility tests, high viscosity, high OH content, contains ricinoleic acid
Cottonseed oils	Contain oleic and linoleic (unsaturated) acids
Peanut oils	
Corn oil	
Sesame oil	
Sunflower oil	
Olive oil	
Palm oil	Contain linolenic (unsaturated) acid
Linseed oil	
Perilla oil	
Soybean oil	
Hempseed oil	Contain erucic acid
Rapeseed oil	
Mustard oil	
Ravison oil	

TABLE 33-5 PHYSICAL CHARACTERISTICS OF SOME FATS AND OILS

<i>Oil or Fat</i>	<i>Iodine Value</i>	<i>Saponi- fication Value</i>	<i>Titer °C</i>	<i>Refractive Index at 25°C</i>
Castor	81-91	176-187	—	1.473-1.477
Coconut	7.5-10.5	250-264	20-24	1.448-1.450*
Corn	103-128	187-193	14-20	1.470-1.474
Cottonseed	99-113	189-198	30-37	1.463-1.472
Kapok	86-110	189-197	27-32	1.468-1.473
Linseed	170-204	188-196	19-21	1.477-1.482
Olive	80-88	188-196	17-26	1.466-1.468
Palm	44-54	195-205	40-47	1.453-1.456*
Palm Kernel	14-23	245-255	20-28	1.449-1.457*
Peanut	84-100	188-195	26-32	1.466-1.470
Perilla	193-208	188-197	—	1.480-1.482
Rapeseed	97-108	170-180	11-15	1.464-1.468
Safflower	140-150	188-194	—	1.473-1.476
Sesame	103-116	188-195	20-25	1.470-1.474
Soybean	120-141	189-195	21-23	1.471-1.475
Sunflower	125-136	188-194	16-20	1.471-1.475
Teaseed	80-90	188-196	13-18	1.466-1.469
Tung	160-175	189-195	—	1.516-1.520
Butterfat	26-42	210-233	33-38	1.453-1.456*
Chicken Fat	64-76	194-204	—	1.452-1.460
Lard	52-77	190-202	32-43	1.459-1.461*
Tallow-Beef	40-48	190-199	40-47	1.450-1.458*
Tallow-Mutton	35-46	192-197	43-48	—

\* at 40°C

## COTTONSEED OIL

## (Halphen Test)

**Procedure**<sup>1</sup>—Mix about 10 ml of sample in a 25 x 250 mm test tube with an equal volume of reagent. The reagent is prepared by mixing equal volumes of amyl alcohol with carbon disulfide containing 1% sulfur. Shake and heat gently in hot water until forming stops. Place the tube in a bath at 110° to 115°C and maintain at that temperature for 1-2 hours. A red color in the solution at the end of the test indicates the presence of cottonseed oil. The intensity of the red color is a rough approximation of the amount of cottonseed oil in the sample. If appreciable quantities of cottonseed oil are present in the sample a positive reaction will usually appear in less than one hour. However, if the quantity of cottonseed oil is small a 2 hour period is essential. The intensity of the red color is reduced by certain processing operations such as hydrogenation and heating and it may be destroyed entirely. Kapok oil reacts to this test with an equal or greater intensity than does cottonseed oil.

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KAPOK OIL<sup>13</sup>

(Besson Test)

The Besson test should be applied only to samples which have been refined with alkali and filtered with diatomaceous earth. Cottonseed oil sometimes produces a deep red color with the Besson test, therefore, it is necessary that care be taken in the interpretation of results, especially when dealing with small amounts of kapok oil. Usually cottonseed oil and other vegetable oils will produce only a deep yellow color under the conditions described.

*Procedure.*—Place 5–10 ml. of the oil or melted fat in a test tube of convenient size and add a volume of chloroform slightly greater than the volume of the sample. Shake until the sample is in solution and then add an amount of silver nitrate reagent (2%  $\text{AgNO}_3$  in absolute alcohol) equal in volume to that of the sample. Shake the mixture for 30 seconds and allow it to stand for 30 minutes. At the end of 30 minutes, if kapok oil is present, the solution will have assumed a brownish-black turbid appearance. In the case of very small amounts of kapok oil, only a deep reddish-brown color will be noticed.

## SESAME OIL

(Villavecchia Test)

*Procedure.*<sup>1</sup>—Mix about 10 ml. of the oil or liquified fat with an equal volume of concentrated hydrochloric acid in a test tube. Add to this mixture 0.1 ml. of a reagent consisting of two ml. of furfural plus 100 ml. of 95% alcohol. Shake well for 15 seconds and allow to stand until the emulsion has broken. Then observe the color of the lower layer as soon as possible. If no pink or crimson color appears the test is negative. If any color is observed in the lower layer add 10 ml. of distilled water, shake again and observe the color as soon as the layers are separated. If the color persists sesame oil is present. If the color disappears sesame oil is absent.

This test is applicable to hydrogenated as well as unhydrogenated oils, although not with the same degree of sensitivity. The sensitivity of the test may be improved by increasing the amount of reagent up to one ml. However, this hastens the rate of color development and it also hastens the amount of non-characteristic colors formed by making the differentiation more difficult.

PEANUT OIL<sup>14</sup>

(Bellier Test—Qualitative)

This method is limited to the detection of peanut oil in cottonseed, soybean, olive or corn oils.

*Procedure.*—Weigh 0.92 grams of sample into a 125-ml. Erlenmeyer flask. Saponify the fat by boiling gently under a reflux condenser with 5 ml. of 1.5 *N* alcoholic potassium hydroxide for five minutes. Then add 50-ml. of 70% alcohol and 0.8 ml. of hydrochloric acid (sp. gr. 1.16). Warm the solution to dissolve any precipitate that may form. Insert a thermometer and cool with continuous agitation at the rate of 1°C. per minute. Observe the temperature at which cloudiness appears. The presence of peanut oil in olive oil is indicated if turbidity appears above 9°C.

The presence of peanut oil in cottonseed soybean or corn oil is indicated if turbidity appears above 13°C

### PEANUT OIL<sup>14</sup>

(Renard Method—Quantitative)

**Procedure**—Weigh 20 g of the sample into an Erlenmeyer flask and saponify the oil or fat by boiling with about 200 ml of alcoholic potassium hydroxide (40 g/liter) under a reflux condenser for 1 hour. After saponification cool the soap solution and then exactly neutralize it with acetic acid (1 + 3 v/v) using phenolphthalein as the indicator. Into an 800–1000 ml flask place 100 ml of distilled water and 120 ml of 20% lead acetate solution. Heat this solution to boiling. Transfer the neutralized soap solution to the 800–1000 ml flask and continue boiling for 1 minute. Cool the flask and contents by immersion in water swirling the flask occasionally to cause the lead soaps to adhere to the sides of the flask. When the contents of the flask have cooled decant the water and excess lead acetate solution and then wash the lead soaps with cold water and 90% alcohol. Add 200 ml of ethyl ether insert a cork stopper and allow the mixture to stand until the soap disintegrates. Heat the mixture on a water bath under a reflux condenser and allow it to boil for about 5 minutes. In the case of soft fats most of the soap will be dissolved but fats containing significant quantities of stearin may not be completely soluble. Cool the ether solution of soaps to 15°–17°C and allow it to stand until all of the insoluble soaps have separated.

Remove the precipitate by filtration using a Buchner funnel and wash the soaps on the filter paper thoroughly with ether. Transfer the ether insoluble lead soaps into a separatory funnel with the aid of a jet of ethyl ether alternating with hydrochloric acid (1 + 3 v/v) if some of the soap adheres to the paper at the end of the operation. Add sufficient hydrochloric acid to make the total volume of acid about 200 ml and enough ethyl ether to make the total volume of ether 150–200 ml. Shake the solution vigorously for several minutes. Allow the layers to separate and drain off the lower acid layer. Wash the ether once with 100 ml of dilute hydrochloric acid and then with several portions of distilled water until the water washings are no longer acid to methyl orange. If some solid particles remain after the third washing with water decompose them by drawing off almost all of the water layer adding a little dilute hydrochloric acid and shaking then continue washing with water as before. Evaporate the ether from the solution of insoluble fatty acids and dry the latter by evaporation on a steam bath after the addition of a few ml of absolute alcohol. Dissolve the dry fatty acids in 100 ml of 90% alcohol using heat if necessary to effect solution. Cool the solution slowly to 15°C, shaking to aid crystallization. Allow the solution to stand for 30 minutes at 15°C.

If peanut oil is present crystals of arachidic acid will separate from the solution. Remove the arachidic acid by filtration washing the precipitate twice with 10 ml of 90% alcohol and then with 70% alcohol. Be sure to maintain the crystals and wash solutions at a definite temperature in order that the solubility corrections given below may be applicable. Dissolve the arachidic acid crystals with boiling absolute alcohol and then remove the alcohol by evaporation. Dry the crystals to constant weight in an air oven and weigh.

Correct the weight of the residue for the solubility of arachidic acid in 90% alcohol. If the washing is performed at 15°C add 0.0025 g/10 ml of 90% alcohol



used for crystallizing and washing; and if at 20°C., add 0.0045 g./10 ml. of 90% alcohol used for crystallizing and washing. The melting point of the arachidic acid so obtained is 71–72°C. To determine the approximate quantity of peanut oil, multiply the corrected weight by 20.

### TEASEED OIL

(Modified Liebermann-Burchard Test)

*Procedure.*<sup>1</sup>—Place exactly 0.8 ml. of acetic anhydride, 1.5 ml. of chloroform and 0.2 ml. of sulfuric acid (sp. gr. 1.84) in a test tube. Mix the contents of the tube and then cool to 5°C. Add 7 drops of sample. Again mix and maintain the mixture at 5°C. for 5 minutes. Should any cloudiness appear add acetic anhydride dropwise, shaking after the addition of each drop until the turbidity disappears. Add 10 ml. of cold (5°C.) ethyl ether, insert a stopper and invert the test tube immediately. Replace the tube in the ice-water bath and observe the color. The presence of teaseed oil is indicated by an intense red color which appears within one minute, reaching a maximum and then fading away.

### MARINE OIL <sup>5</sup>

(Insoluble Bromide Test)

The insolubility of the bromides of the highly unsaturated fatty acids is made use of as a means of detecting unhydrogenated fish oil. The following procedure is applicable to the detection of fish oil in animal and vegetable fats and oils, providing metallic salts are absent. This method is very sensitive.

*Procedure.*—Place above 5 g. of sample in a test tube containing 12 ml. of a mixture of equal parts (v/v) of chloroform and acetic acid. Add bromine, dropwise, until a slight excess is indicated by the color, keeping the solution at about 20°C. Allow the tube and contents to stand for 15 minutes or more, then place in boiling water. If vegetable oils only are present, the solution will be perfectly clear, while if fish oils are present, it will become cloudy due to the presence of insoluble bromides.

### TRISTEARIN FATS IN PORK FATS

(Bömer Value)

The method for detecting the presence of beef fat and other fats containing tristearin in lard is due to Bömer<sup>15</sup> and the values obtained by applying this method are frequently referred to as Bömer numbers or values. The procedure is based on the difference between the melting point of glycerides and the melting point of the corresponding fatty acids. This difference is large for pure hog fat (unhydrogenated) and small for tallow. The method is inapplicable when hydrogenated pork fat is present.

The Bömer value, if carefully determined, will permit the detection of 10% beef fat in lard in almost all cases, and it frequently will enable detection of as little as 5%. However, no quantitative significance should be attached to the results of this determination, that is, one cannot estimate from the Bömer value how much beef fat is present in a given sample. There is a general correlation between the melting point of the glycerides and the presence of beef fat, but it is inadvisable to accept this as a definite criterion.

<sup>15</sup> Bömer, A., Z. Unters. Nahr. Genussm., 26, 559, 1913.

## CHEMICAL CHARACTERISTICS OF FATS

SAPONIFICATION VALUE<sup>1</sup>

The saponification value is a measure of the amount of alkali required to saponify a given weight of fat. It is, therefore, a measure of molecular weight. The saponification value, sometimes referred to as the Koettsdoerfer number, is expressed as the milligrams of potassium hydroxide required to saponify 1 g. of fat. The procedure given below is applied to normal fats and oils and commercial fatty acids.

**Reagent.**—Add 5–10 g. of potassium hydroxide to 1 liter of 95% ethyl alcohol and boil the mixture under a reflux condenser for about 1 hour. Then distill and collect the alcohol and cool it to below 15.5°C. Maintain the alcohol at this temperature during the process of dissolving the potassium hydroxide. To 1 liter of the cooled alcohol add about 40 g. of potassium hydroxide. Allow to stand with occasional shaking until the alkali is dissolved. The solution should remain clear.

**Procedure.**—Weigh a sample of such quantity that there will be an excess of reagent of about 50%. When 50 ml. of reagent are used this will usually require 4–5 g. of sample. Saponification should be conducted in alkali-resistant Erlenmeyer flasks of about 250- or 300-ml. capacity. Add 50 ml. of the alcoholic alkali solution to the flask containing the sample and the same amount to one or more empty flasks to serve as blank determinations.

Attach condensers to the flasks containing sample and blanks and boil gently but steadily until saponification is complete. Make certain that the vapor ring in the condenser does not rise to the top of the condenser while the solution is boiling or there may be some loss. Saponification usually requires about 1 hour, but in some cases more time is required. There is no way to determine when saponification is complete except to run a series of samples at increasing saponification intervals, continuing this until the values obtained become constant.

When saponification is complete allow the solution to cool somewhat and then wash down the inside of the condenser with a small amount of distilled water. Disconnect the condenser, add about 1 ml. of phenolphthalein (1% in 95% alcohol) and titrate the solution with 0.5 *N* hydrochloric acid until the pink color just disappears.

$$\text{The saponification value} = \frac{28.05 \times (B - S)}{\text{Wt. of sample}},$$

where *B* = titration of blank, and

*S* = titration of sample.

## HYDROXYL VALUE

The hydroxyl value is a measure of the hydroxyl groups in a given substance and it is defined as the milligrams of potassium hydroxide equivalent to the hydroxyl content of one gram of sample. The presence of hydroxyl groups in natural fats is due largely to the presence of substances such as glycerol, mono- and diglycerides and sterols. The natural fats with the exception of castor oil contain essentially no hydroxy acids.

The hydroxyl value or the acetyl value as it was formerly designated was for many years determined by the acetylation of fat with acetic anhydride. The hy-

3. The thiocyanogen value<sup>18</sup> is a special measure of unsaturation which, when used in conjunction with the iodine value, permits calculation of fatty acid composition. In all cases results are calculated in term of equivalent iodine. Ultra-violet absorption spectroscopy has replaced the thiocyanogen method to a large extent.

All standard methods for determining iodine value are based on the addition of an excess of halogen reagent followed by titration of the unreacted halogen. From the amount of halogen absorbed, the unsaturation is calculated. The iodine value is expressed in terms of centigrams of iodine absorbed by 100 g. of fat. The determination is satisfactory for compounds containing only isolated double bonds, but in the case of compounds containing conjugated bonds, absorption is not complete. In the application of the standard Wijs method to fats and oils containing conjugated double bonds, the conditions are arbitrarily established and the results are, therefore, empirical.

A variety of methods are available for determining iodine values of fats but the Wijs<sup>19</sup> and Hanus,<sup>20</sup> and possibly the Kaufmann<sup>21</sup> methods are the most commonly used. The Kaufmann method is used extensively in Germany and other parts of Europe. The Wijs procedure is given here.

**Reagent.**—The Wijs reagent is an 0.2 *N* solution of iodine monochloride in glacial acetic acid. Iodine monochloride is available commercially and this grade has been found to be satisfactory. Wijs solution may be prepared by chlorinating and adjusting a solution of iodine in glacial acetic acid but this method of preparation and the subsequent adjustment are tedious.

Prepare a stock solution by adding  $317 \pm 0.1$  g. of iodine monochloride to one liter of glacial acetic acid (A.C.S. grade). Filter this solution rapidly through filter paper into a clean, dry bottle. Prepare the Wijs reagent by adding  $117 \pm 0.1$  ml. of the stock solution to a 5-lb. bottle of glacial acetic acid (A.C.S. grade). The stock and Wijs solutions should be stored in a dark area at a temperature not greater than 30°C. Mix the Wijs solution well and determine the halogen ratio as follows:

**Iodine Content.**—Pour 150 ml. of saturated chlorine water into a 500-ml. Erlenmeyer flask and add some glass beads. Pipet 5 ml. of the Wijs solution into the flask containing the saturated chlorine water. Shake and heat to boiling. Boil briskly for 10 minutes, cool, and add 30 ml. of 2% sulfuric acid and 15 ml. of 15% potassium iodide solution. Mix well and titrate immediately with 0.1 *N* sodium thiosulfate solution to a starch end point.

**Total Halogen Content.**—Pour 150 ml. of recently boiled distilled water into a clean, dry 500-ml. Erlenmeyer flask. Add 15 ml. of 15% potassium iodide solution. Pipet 20 ml. of Wijs solution into the flask and mix well. Titrate immediately with 0.1 *N* sodium thiosulfate solution to a starch indicator end point.

$$\text{Halogen ratio} = \frac{2A}{3B - 2A},$$

where *A* = titration of iodine content and

*B* = titration of total halogen content.

<sup>18</sup> Kaufmann, H. P., *Chem.-Ztg.*, 49, 768, 1925.

<sup>19</sup> Wijs, J. J. A., *J. Soc. Chem. Ind.*, 17, 698, 1898.

<sup>20</sup> Hanus, J., *Z. Untersuch Nahr., und Genussmittel*, 1, 913, 1901.

<sup>21</sup> Kaufmann, H. P., *Studien auf dem Fettgebiet*, Verlag Chemie, G.m.b.H. Berlin, 1953.

Remove the flask from storage. Add 20 ml. of 15% aqueous potassium iodide solution (w/v) and 100 ml. of distilled water. Titrate the solution with 0.1 *N* sodium thiosulfate solution adding the latter gradually and with constant and vigorous shaking. Continue the titration until the yellow color has almost disappeared. Add 1 to 2 ml. of starch indicator solution (10 g./liter) and continue the titration until the blue color has just disappeared.

$$\text{The iodine value} = (B - S) \times N \times 12.69,$$

where *B* = titration of blank,

*S* = titration of sample, and

*N* = normality of sodium thiosulfate solution.

The absorption time may be shortened from 30 to 3 minutes for fats containing only isolated double bonds by adding immediately after addition of the reagent 10 ml. of a solution of 2.5% mercuric acetate in glacial acetic acid. Although this is not part of the standard method, the practice is common, especially for production control purposes.

The relation between weight of the sample and % excess reagent depends upon the iodine value and the concentration of the ICl reagent. The calculation is:

$$\text{Required weight of sample in grams} = \frac{K \times \text{titration of blank (ml. 0.1 } N \text{ Na}_2\text{S}_2\text{O}_3)}{\text{Iodine value}},$$

where *K* = 0.6346 for 100% excess,

*K* = 0.5904 for 115% excess,

*K* = 0.5400 for 135% excess, and

*K* = 0.5076 for 150% excess.

When the blank titration is 50.0 ml., i.e., the reagent is exactly 0.2 *N*, these equations simplify to:

$$\text{The required weight of sample for 100\% excess} = \frac{31.73}{\text{I.V.}}$$

$$\text{The required weight of sample for 115\% excess} = \frac{29.52}{\text{I.V.}}$$

$$\text{The required weight of sample for 135\% excess} = \frac{27.00}{\text{I.V.}}$$

$$\text{The required weight of sample for 150\% excess} = \frac{25.38}{\text{I.V.}}$$

### DIENE VALUE

*Procedure.*<sup>1</sup>—Weigh  $3 \pm 0.001$  g. of sample into a dry Erlenmeyer flask, and add 25.0 ml. of maleic anhydride-toluene reagent (6 + 94, w/w). Place a small boiling stone in the flask and attach an air condenser. Heat so as to reflux gently and continue for 3 hours. Prepare and conduct a blank determination similar to and simultaneously with the sample. After refluxing, add 5 ml. of freshly boiled and cooled distilled water through the condenser and reflux for an additional 15 minutes. Remove the flask and attached condenser from the heat source, allow to cool, and then add 5 ml. of ethyl ether and 10 ml. of water through the condenser,

Disconnect the condenser and wash down the condenser joint with ten ml of water, allowing the washings to run into the flask

Carefully transfer the contents of flask into a 250 ml separatory funnel. Wash the flask with three 15 ml portions of ether followed by three 15 ml portions of water, adding both ether and water washings to the separatory funnel. Stopper the funnel, shake the contents vigorously for one minute, remove the stopper and allow the layers to separate. If any evidence of emulsion is present, add a few drops of alcohol, swirl gently, and then allow to stand until two clear layers have formed. Draw off the lower aqueous layer into a 500 ml Erlenmeyer flask. Repeat the extraction with one 25 ml portion of water and follow with four extractions using 10 ml portions of water for each. Break up any formation of emulsion with a few drops of alcohol. Test a portion of the sixth extraction for acidity with methyl orange indicator. If there is any evidence of acidity, continue extracting until the extract is neutral. Titrate the combined extracts with 0.1 *N* sodium hydroxide solution using phenolphthalein indicator.

$$\text{The diene value} = \frac{(B - S) \times N \times 12.69}{\text{Wt. of sample}}$$

where *N* = normality of sodium hydroxide,

*B* = titration of blank, and

*S* = titration of sample

## PHYSICAL CHARACTERISTICS OF FATS

### MELTING POINT

#### CLOSED CAPILLARY TUBE METHOD

When solid natural fats are heated slowly they pass through a stage of gradual softening before becoming completely liquid. The phase transformation is not definite and sharp as it is in the case of substances consisting of only a single constituent. The melting point is an arbitrary value depending upon the method by which it is determined. The value obtained by the conventional closed capillary tube method represents the melting point of the highest melting phase.

*Procedure 1*—Dip 3 clean capillary glass tubes (1 mm I.D., 2 mm O.D.) in a melted and filtered portion of the sample so that about a 1 cm column of fat is retained in each tube. Fuse the ends of the tubes at which the fat is located but avoid hurting any of the fat. Maintain the tubes at a temperature of 4°–10°C for 16 hours.

Attach the tubes to a thermometer (0–65°C, in 0.2°C subdivisions, A.O.C.S. Specification H-6-40) so that the fat is adjacent to the bulb of the thermometer. Place the thermometer and tubes in a 600 ml glass beaker containing clear water so that the bottom of the bulb of the thermometer is immersed about 3 cm in the water. The temperature of the water at the start should be about 10°C below the melting point of the fat.

Agitate the bath gently and apply heat so that the temperature of the water increases at about 0.5°C per minute. The melting point is the temperature at which the fat in the tubes becomes entirely clear. It is advisable to average the temperature of the melting points of several tubes on the same sample.

*Procedure for Unstable Polymorphic Forms.*—Fill several capillary tubes and solidify the fat in the usual manner. Place the tubes one into each of several liquid baths maintained in an ascending series of temperatures. The lowest temperature at which the sample liquefies is the melting point.

#### WILEY METHOD

The Wiley melting point method involves heating a disc of solidified fat until the disc assumes a spherical shape. At this point the fat is assumed to be completely liquid. Actually the final shape may be somewhat oval or elliptical rather than spherical. Some analysts use as the criterion of melting, the temperature at which the specimen is entirely clear. This is usually somewhat higher than the temperature at which an oval shape is reached. The determination of the end point is a critical part of this method.

*Procedure.*<sup>1</sup>—Boil 95% alcohol and distilled water separately for 10 minutes to eliminate dissolved gases. Fill a large test tube (300 mm. long by 35–38 mm. i.d.) to a height of 2–3 inches with hot water and then add approximately an equal amount of hot alcohol. Tilt the tube at an angle of about 45° and pour the liquid slowly and carefully down the inside of the tube to avoid the entrainment of air and also to minimize mixing of the alcohol and water. Either of these may render the mixture unsatisfactory for use.

Provide an aluminum (or steel) plate about 4" x 4", 1/8" thick, through which 3/8" holes are drilled. Chill the metal plate thoroughly in a refrigerator (8° to 10°C.) and place it on a cold, flat surface such as a glass plate before filling the holes with dry, melted and filtered sample. After filling, allow the plate to remain in the refrigerator for at least 2 hours.

Cut off the excess sample protruding above the level of the plate, remove a disc and drop it into the alcohol-water mixture in the large test tube which has been previously cooled to at least 10°C. below the melting point of the sample. The disc will drop to the approximate interface between the two liquids. Place the test tube in a beaker (200 mm. high, about 85 mm. diam.) containing cold water.

Insert a thermometer (0–65°C., in 0.2° subdivisions; AOCS Specification H 6-40) until the bulb is just above the fat disc. Rotate the thermometer slowly around the disc to maintain a uniform temperature while heat is applied under the beaker. Make certain the disc does not touch the side of the test tube or the thermometer. Heat the bath slowly and agitate it continuously with a small stream of air. As the temperature of the alcohol-water mixture rises, the fat disc will gradually change shape. As it begins to do this, lower the thermometer until the center of the bulb is in the same horizontal plane as the disc. Continue rotating the thermometer and regulate the rate of heating so that about 10 minutes are required for an increase of 2°C. in temperature. Observe the temperature at which the fat disc becomes spherical. This is the Wiley melting point. At this point the temperature of the water bath must not be more than 1.5°C. above the melting point of the sample. The first determination is exploratory to establish the range of conditions and should be followed by one or more determinations conducted in accordance with the conditions established.

## SOFTENING POINT

## OPEN CAPILLARY TUBE METHOD

The softening point also referred to as the open end capillary melting point, the rise melting point and the slipping point indicates the temperature at which the sample has softened sufficiently to be forced upward in a capillary tube by the hydrostatic pressure of water.

**Procedure**<sup>1</sup>—Melt and filter the fat to remove impurities and moisture. Dip at least 3 clean capillary tubes (1 mm I.D. 3 mm O.D.) into the liquid sample so that a column about 1 cm is retained when the tube is removed. Cause the fat to solidify by holding the ends of the tubes containing the sample pressed against a piece of ice. Place the tubes in a container with a tight cover and hold in a refrigerator at 4°–10°C for 16 hours.

Remove the tubes from the refrigerator and attach with a rubber band or by any other suitable means to a thermometer (0–60°C in 0.2°C subdivisions AOCs Specification H 640) so that the lower ends of the tubes are even with the bottom of the mercury bulb of the thermometer. Suspend the thermometer in a 600-ml beaker containing clear distilled water. Immerse the thermometer in the water so that the bottom of the bulb is about 3 cm below the surface of the water. Adjust the starting temperature of the water to 8° to 10°C below the softening point of the sample. Agitate the water with a small stream of air or by some other suitable means and apply heat so as to increase the bath temperature at the rate of 1°C per minute slowing down to 0.5°C per minute as the softening point is approached. Continue heating until the fat column rises in each tube. Observe the temperature at which each column rises and calculate the average of all tubes.

## CONGEAL POINT

The congeal point as applied to fats is a measure of the solidification temperature. It differs from the titer point in that the former is a measure of solidification temperature of the fatty acids while the congeal point pertains specifically to the fats. The primary use of the congeal point is for hydrogenation control although it is also employed in some purchase specifications. The congeal point is a simple test and rapid to perform but the reproducibility between laboratories leaves something to be desired.

**Apparatus**—Provide a temperature controlled air bath by centering and supporting a 500 ml stainless steel beaker containing sufficient lead shot to provide a satisfactory ballast within a 4000 ml beaker. Water or ice and water is maintained in the large beaker to control the air temperature within the smaller beaker. The 500 ml beaker should be fitted with a cover having a centered opening to hold the 180 ml beaker. Provide also a 2000 ml glass beaker containing water to serve as a cooling bath. Mount a 100 watt electric light about 1 inch behind the bath centered 1 to 2 inches below the level of water in the outer beaker and in a horizontal plane with the center of the 180 ml beaker and eye level.

**Procedure**<sup>1</sup>—Heat 89–91 g of the sample to 130°C in a 180 ml beaker (electrolytic type) stirring continuously during this entire period. It is necessary that all water be removed.

Remove the beaker and contents from the heat source and allow the fat to cool to 65°C. Then place the beaker and sample in a 2000 ml beaker containing water adjusted to 15°C  $\pm$  0.5°C for congeal points below 35°C or 20°C  $\pm$  0.5°C for

congeal points at 35°C. or above. Adjust so that the fat level is about 6 mm. below the water level.

Stir the sample with a thermometer (0° to 65°C., in 0.2° subdivisions; AOCS Specification H 6-40) at 250 r.p.m. rubbing the thermometer against the sides and bottom of the beaker until the cloud point is reached. This is the point at which the immersed section of the thermometer is visible when placed in the center of the beaker but invisible when placed at the back of the beaker. It is important to avoid too rapid crystal growth at this stage so the beaker should be removed from the water bath and then returned to it at short intervals. A good rule is to immerse the beaker about 75% of the time until the first crystals form and about 25% of the time thereafter and until the cloud point is reached.

Immediately transfer the beaker and contents to the air bath which is maintained at 20°C. Secure the thermometer in the center of the sample by means of a one-hole stopper. Observe the temperature every minute, but do not disturb the sample during this period. The maximum temperature attained is the congeal point.

The temperatures of 20°C. and 15°C. specified for the air and water baths may require adjustment depending upon the composition and the hardness of the sample but these suffice for most fats to which this determination is applied.

### TITER POINT

The titer point is a measure of the solidification temperature of fatty acids. It is useful for grading hard fats such as fully hydrogenated fats and oils. It is also employed for grading fats utilized in the production of soaps.

**Procedure.<sup>1,5</sup>**—Weigh about 110 g. of glycerol-potassium hydroxide (5 + 1, w/w) into a beaker, flask or casserole of adequate capacity. Heat and stir the mixture until the temperature reaches 150°C. Add 40–50 ml. of oil or melted fat and reheat to 140–150°C. Continue stirring at this temperature (not above 150°C.) until saponification is complete which is usually indicated by a homogeneous appearance of the solution and by copious soap bubbles rising from the surface of the solution.

Add carefully while stirring 50 ml. of dilute sulfuric acid (30% w/w). Continue stirring until the fatty acids have completely separated and are liquid and clear.

Add 200–300 ml. of distilled water and boil for 2–3 minutes. Remove the aqueous layer carefully to avoid loss of any fatty acids. Wash again with distilled water and continue until the washings are neutral to methyl orange indicator. Two or three washings are usually sufficient.

Collect and filter the fatty acids to remove any water that may be present. Finally heat the acids on a hot plate at 130°C. for a moment to remove traces of water. Transfer the fatty acids to a test tube (100 mm. ht., 25 mm. diam.) with an etched mark 57 mm. from the bottom of the tube and fill to the mark. Insert a thermometer (0–65°C., in 0.2°C. subdivisions; AOCS Specification H 6-40), equidistant from the sides and to the immersion mark on the thermometer. Place the test tube containing the sample in a bath assembled as shown in Fig. 33-4. This provides a water-cooled air bath in which the fatty acids are solidified. It helps to add some lead shot to the bottom of the bottle to serve as ballast. The bath is maintained at 15–20°C. below the titer point at all times. For titers so low that ice and water will not provide sufficiently low bath temperatures, crushed dry ice and ethylene glycol may be used instead. The liquid level in the bath should be maintained 1 cm. above the level of the fatty acids in the test tube.



The stirrer should move through a vertical distance of about 38 mm, at the rate of 100 complete motions per minute

Stir as indicated until the temperature remains constant for 30 seconds or begins to rise in less than a 30 second interval. At this point discontinue stirring immedi-

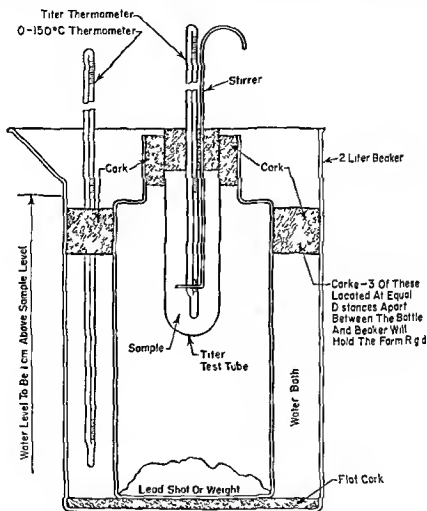


FIG. 53.4 Titer Stirring Assembly

ately remove the stirrer and observe the increase in temperature. The titer point is the highest temperature reached during this rise.

### CLOUD POINT

The cloud point is the temperature at which crystallization begins when a liquid fat is cooled and agitated under standardized conditions. The cloud point is related to hard fat content and it is therefore, a useful test with which to follow the progress of hydrogenation.

**Procedure**<sup>1</sup>—The sample must be completely dry before making the test. Heat 60 to 75 g of sample to 130°C immediately before making the test. Pour about

45 ml. of the heated fat into a 4-oz. oil sample bottle. Begin to cool the bottle and contents in a water bath, stirring with a thermometer just enough to keep the temperature uniform. When the temperature of the fat is about  $10^{\circ}\text{C}.$  above the cloud point, begin stirring steadily and rapidly in a circular motion to prevent supercooling and solidification of fat crystals on the sides or bottom of the bottle. From this time on, do not remove the thermometer from the sample, since to do so may introduce air bubbles which will interfere with the test. The bottle is maintained in such a position that the upper levels of the sample in the bottle and the water in the bath are about the same. Remove the bottle from the bath and inspect the sample regularly. The cloud point is the temperature at which that portion of the thermometer immersed in the oil becomes invisible when viewed horizontally through the bottle and sample.

### COLD TEST

The cold test is a measure of the time required for a given oil to crystallize under arbitrarily fixed conditions. This test is designed to evaluate the suitability of salad oil for use in mayonnaise which requires oils that do not deposit stearin at refrigerator temperatures.

*Procedure.*<sup>1</sup>—All traces of moisture must be removed and preformed crystal nuclei must be destroyed before this test is started. For this purpose, filter the sample through a filter paper and then heat the filtered portion to  $130^{\circ}\text{C}.$  If the moisture is not removed cloudiness will result on chilling. If the nuclei are not destroyed, crystallization will be premature.

Fill a 4-oz. oil sample bottle completely full with the sample and tightly insert a cork stopper. Adjust the temperature to  $25^{\circ}\text{C}.$  in a water bath and then seal the stopper with paraffin. Immerse the bottle and sample in an ice and water bath and make certain that the entire bottle is covered with water and cracked or clipped ice. The bath must be packed with ice and the ice replenished as often as necessary to keep the temperature of the bath at  $0^{\circ}\text{C}.$

Remove the bottle from the bath after 5.5 hours and examine the oil closely for fat crystals or cloudiness. Do not mistake small and finely dispersed air bubbles for fat crystals. To pass the test, the sample must be clear, limpid, and brilliant at 5.5 hours.

### REFRACTIVE INDEX

The refractive index of fats is closely related to the molecular structure and unsaturation of these materials. As applied to the analysis of fats, the refractive index is used as a *fat constant*, as a measure of unsaturation, as a means of determining the fat content of certain source materials, and as a control test for hydrogenation and certain other plant processes.

The Butyro and Abbe scales are both employed for the determination of refractive index but the former has the advantage of providing slightly greater precision. The relation between Butyro scale readings and refractive indices are given in Table 33-8.

The refractive index of a given substance decreases with increasing wavelength of the illuminating light and with increasing temperature of reading. Ordinarily a monochromatic lamp (sodium D line) is employed to illuminate the scale. It is preferable to maintain the temperature of the refractometer at the specified level by the use of a constant temperature water bath and a circulating device to circulate water through the instrument. The refractive indices of oils are usually deter-

TABLE 33.8 BUTYRO-REFRACTOMETER READINGS AND INDICES OF REFRACTION<sup>a</sup>

Refractive Index $n_d$	Fourth Decimal of $n_d$									
	0	1	2	3	4	5	6	7	8	9
<i>Butyro Scale Readings</i>										
1.422	0.0	0.1	0.2	0.4	0.5	0.6	0.7	0.9	1.0	1.1
1.423	1.2	1.4	1.5	1.6	1.7	1.9	2.0	2.1	2.2	2.4
1.424	2.5	2.6	2.7	2.8	3.0	3.1	3.2	3.3	3.5	3.6
1.425	3.7	3.8	4.0	4.1	4.2	4.3	4.5	4.6	4.7	4.8
1.426	5.0	5.1	5.2	5.4	5.5	5.6	5.7	5.9	6.0	6.1
1.427	6.2	6.4	6.5	6.6	6.8	6.9	7.0	7.1	7.2	7.4
1.428	7.5	7.6	7.7	7.9	8.0	8.1	8.2	8.4	8.5	8.6
1.429	8.7	8.9	9.0	9.1	9.2	9.4	9.5	9.6	9.8	9.9
1.430	10.0	10.1	10.3	10.4	10.5	10.6	10.7	10.9	11.0	11.1
1.431	11.3	11.4	11.5	11.6	11.8	11.9	12.0	12.2	12.3	12.4
1.432	12.5	12.7	12.8	12.9	13.0	13.2	13.3	13.5	13.6	13.7
1.433	13.8	14.0	14.1	14.2	14.4	14.5	14.6	14.7	14.9	15.0
1.434	15.1	15.3	15.4	15.5	15.6	15.8	15.9	16.0	16.2	16.3
1.435	16.4	16.6	16.7	16.8	17.0	17.1	17.2	17.4	17.5	17.6
1.436	17.8	17.9	18.0	18.2	18.3	18.4	18.5	18.7	18.8	18.9
1.437	19.1	19.2	19.3	19.5	19.6	19.7	19.8	20.0	20.1	20.2
1.438	20.4	20.5	20.6	20.8	20.9	21.1	21.2	21.3	21.4	21.6
1.439	21.7	21.8	22.0	22.1	22.2	22.4	22.5	22.6	22.7	22.9
1.440	23.0	23.2	23.3	23.4	23.5	23.7	23.8	23.9	24.1	24.2
1.441	24.3	24.5	24.6	24.7	24.8	25.0	25.1	25.2	25.4	25.5
1.442	25.6	25.8	25.9	26.1	26.2	26.3	26.5	26.6	26.7	26.9
1.443	27.0	27.1	27.3	27.4	27.5	27.7	27.8	27.9	28.1	28.2
1.444	28.3	28.5	28.6	28.7	28.9	29.0	29.2	29.3	29.4	29.6
1.445	29.7	29.9	30.0	30.1	30.3	30.4	30.6	30.7	30.8	30.9
1.446	31.1	31.2	31.4	31.5	31.6	31.8	31.9	32.1	32.2	32.3
1.447	32.5	32.6	32.8	32.9	33.0	33.2	33.3	33.5	33.6	33.7
1.448	33.9	34.0	34.2	34.3	34.4	34.6	34.7	34.9	35.0	35.1
1.449	35.3	35.4	35.6	35.7	35.8	36.0	36.1	36.3	36.4	36.5
1.450	36.7	36.8	37.0	37.1	37.2	37.4	37.5	37.7	37.8	37.9
1.451	38.1	38.2	38.3	38.5	38.6	38.7	38.9	39.0	39.2	39.3
1.452	39.5	39.6	39.7	39.9	40.0	40.1	40.3	40.4	40.6	40.7
1.453	40.9	41.0	41.1	41.3	41.4	41.5	41.7	41.8	42.0	42.1
1.454	42.3	42.4	42.5	42.7	42.8	43.0	43.1	43.3	43.4	43.6
1.455	43.7	43.9	44.0	44.2	44.3	44.4	44.6	44.7	44.9	45.0
1.456	45.2	45.3	45.5	45.6	45.7	45.9	46.0	46.2	46.3	46.4
1.457	46.6	46.7	46.9	47.0	47.2	47.3	47.5	47.6	47.7	47.9
1.458	48.0	48.2	48.3	48.5	48.6	48.8	48.9	49.1	49.2	49.4
1.459	49.5	49.7	49.8	50.0	50.1	50.2	50.4	50.5	50.7	50.8

TABLE 33-8. (Continued)

Refractive Index $n_d$	Fourth Decimal of $n_d$									
	0	1	2	3	4	5	6	7	8	9
<i>Butyro Scale Readings</i>										
1.460	51.0	51.1	51.3	51.4	51.6	51.7	51.9	52.0	52.2	52.3
1.461	52.5	52.7	52.8	53.0	53.1	53.3	53.4	53.6	53.7	53.9
1.462	54.0	54.2	54.3	54.5	54.6	54.8	55.0	55.1	55.3	55.4
1.463	55.6	55.7	55.9	56.0	56.2	56.3	56.5	56.6	56.8	56.9
1.464	57.1	57.3	57.4	57.6	57.7	57.9	58.0	58.2	58.3	58.5
1.465	58.6	58.8	58.9	59.1	59.2	59.4	59.5	59.7	59.8	60.0
1.466	60.2	60.3	60.5	60.6	60.8	60.9	61.1	61.2	61.4	61.5
1.467	61.7	61.8	62.0	62.2	62.3	62.5	62.6	62.8	62.9	63.1
1.468	63.2	63.4	63.5	63.7	63.8	64.0	64.2	64.3	64.5	64.7
1.469	64.8	65.0	65.1	65.3	65.4	65.6	65.7	65.9	66.1	66.2
1.470	66.4	66.5	66.7	66.8	67.0	67.2	67.3	67.5	67.7	67.8
1.471	68.0	68.1	68.3	68.4	68.6	68.7	68.9	69.1	69.2	69.4
1.472	69.5	69.7	69.9	70.0	70.2	70.3	70.5	70.7	70.8	71.0
1.473	71.1	71.3	71.4	71.6	71.8	71.9	72.1	72.2	72.4	72.5
1.474	72.7	72.9	73.0	73.2	73.3	73.5	73.7	73.8	74.0	74.1
1.475	74.3	74.5	74.6	74.8	75.0	75.1	75.3	75.5	75.6	75.8
1.476	76.0	76.1	76.3	76.5	76.7	76.8	77.0	77.2	77.3	77.5
1.477	77.7	77.9	78.1	78.2	78.4	78.6	78.7	78.9	79.1	79.2
1.478	79.4	79.6	79.8	80.0	80.1	80.3	80.5	80.6	80.8	81.0
1.479	81.2	81.3	81.5	81.7	81.9	82.0	82.2	82.4	82.5	82.7
1.480	82.9	83.1	83.2	83.4	83.6	83.8	83.9	84.1	84.3	84.5
1.481	84.6	84.8	85.0	85.2	85.3	85.5	85.7	85.9	86.0	86.2
1.482	86.4	86.6	86.7	86.9	87.1	87.3	87.5	87.6	87.7	88.0
1.483	88.2	88.3	88.5	88.7	88.9	89.1	89.2	89.4	89.6	89.8
1.484	90.0	90.2	90.3	90.5	90.7	90.9	91.1	91.2	91.4	91.6
1.485	91.8	92.0	92.1	92.3	92.5	92.7	92.9	93.0	93.2	93.4
1.486	93.6	93.8	94.0	94.1	94.3	94.5	94.7	94.8	95.0	95.2
1.487	95.4	95.6	95.8	96.0	96.1	96.3	96.5	96.7	96.9	97.0
1.488	97.2	97.4	97.6	97.8	98.0	98.1	98.3	98.5	98.7	98.9
1.489	99.1	99.2	99.4	99.6	99.8	100.0	—	—	—	—

<sup>22</sup> Elsdon, G. D., *Edible Oils and Fats*, Ernest Benn, London, 1926.

mined at 40°C and the refractive indices of high melting fats are measured at 60°–70°C. The sample must be completely liquid when examined.

When necessary, corrections for variation in temperature may be made according to the following calculation:

$$R = R_1 + \lambda(T_1 - T)$$

$R$  = Reading reduced to temperature  $T$

$R_1$  = Reading at temperature  $T_1$

$T$  = The desired temperature

$T_1$  = The temperature at which reading  $R_1$  is made

$\lambda$  for fats on the Butyro scale = 0.55

$\lambda$  for oils on the Butyro scale = 0.58

$\lambda$  for fats on the Abbe scale = 0.000365

$\lambda$  for oils on the Abbe scale = 0.000385

**Procedure**—Make certain the refractometer is in proper calibration by means of a suitable standard. Glass prisms of known refractive indices are available from instrument suppliers. Liquid standards are also provided.

Be sure the prisms are clean. Place a few drops of the dry sample on the lower prism of the refractometer. Close the prisms tightly, allow a short time for the sample to come to the temperature of the instrument, and then read the refractive index. The fat should be removed after each examination with a small slab of cotton saturated with a suitable solvent such as toluene.

### SOLID FAT INDEX

Dilatometry or dilatometric analysis of fats depends on differences between the specific volumes of the liquid and solid phases. As a sample of fat is melted there is an accompanying increase in specific volume resulting from both thermal expansion and melting dilation. The increase in volume resulting from phase transformation (melting dilation) is considerably greater than the increase in volume caused by thermal expansion. When the volume changes are plotted against temperature the resulting melting dilation curve is roughly similar to the curve shown in Fig. 33.5. The liquid line represents the thermal expansion of the liquid while the solid line represents the thermal expansion of the solid. The curved line joining the liquid and solid lines is the melting curve over which solid is changing to liquid as the temperature is increased.

For purposes of calculating solids, it is assumed that the liquid and solid lines are parallel and that the total increase of units of specific volume from solid to liquid is 0.1 ml per gram. At any temperature the percentage of solids  $\frac{100\lambda}{1}$  or 1000 $\lambda$  when  $\lambda = 0.1$ .

The dilatometric procedure is designed to provide an empirical index of the relative amounts of the liquid and solid fractions in a sample at any selected temperature or over a range of temperatures extending from the apparent solid state to the completely liquid phase. The results of dilatometric analyses are designated by the method of the American Oil Chemists Society as the *solid fat index*.

Others may use the designation, *solid fat content*. The desirability of the latter, however, seems questionable due to the highly arbitrary nature of the method and results.

**Apparatus.**<sup>1</sup>—Pyrex dilatometers with glass stoppers, constructed in accordance with the specifications shown in Fig. 33-6. The stems should be made from precision-bore capillary tubing graduated in 0.005-ml. increments from 0 to 1.400 ml. with an overall accuracy of at least  $\pm 0.005$  ml. The scale should be marked 0 to 1400 in intervals of 50. The dilatometers should have identification numbers on the stems and stoppers. Springs are necessary to attach the stoppers securely to the

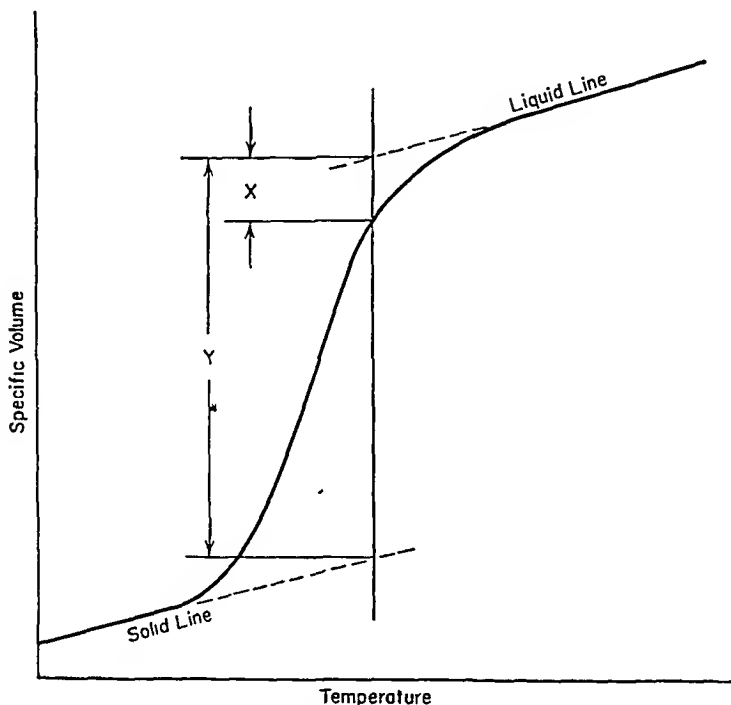


FIG. 33-5. Melting Dilation Curve.

dilatometers. Clamps, thermometer type, are needed for holding the dilatometers in the constant temperature baths.

Constant temperature water baths accurate to  $\pm 0.05^{\circ}\text{C}$ . with provision for adequate circulation. Solid fat indices at  $10^{\circ}$ ,  $21.1^{\circ}$ ,  $26.7^{\circ}$ ,  $33.3^{\circ}$ , and  $37.8^{\circ}\text{C}$ . are commonly used to characterize shortenings and margarine oils. Therefore, the baths required are  $0^{\circ}$ ,  $10^{\circ}$ ,  $21.1^{\circ}$ ,  $26.7^{\circ}$ ,  $33.3^{\circ}$ ,  $37.8^{\circ}$ , and  $60^{\circ}\text{C}$ .

Pyrex 2 mm. I.D. capillary 2-way stopcock with a buret tip.

Check all new dilatometers for accuracy before using. Clean and dry each dilatometer thoroughly and then clamp the dilatometer securely in an inverted position. Attach the capillary stopcock to the end of the stem of the dilatometer and seal the joint with cement (Fisher Pyseal or equivalent).

Allow the cement to harden, and then immerse the tip of the stopcock into a reservoir of clean redistilled mercury which is at room temperature. With the

aid of vacuum draw the mercury into the stem of the dilatometer until the calibrated portion of the stem is full. Withdraw successive 0.200 ml portions of mercury into a tared 50 ml beaker and weigh. The volume in ml contained in each measured scale interval is

$$\frac{\text{Weight of mercury}}{\text{Final} - \text{initial scale reading}} \times \text{sp vol of mercury at } T_R \times 1000$$

where  $T_R$  is room temperature and

$$1 \text{ ml} = 1000 \text{ in scale reading}$$

In order to comply with the specifications of the method 1 scale division is the maximum allowable overall tolerance. A correction curve may be used with dilatometers which do not comply.

**Procedure 1**—Deaerate about 50 ml of the indicator solution (1% potassium dichromate in distilled water) for 3 minutes in a 250 ml filter flask or other convenient container at a pressure slightly above the vapor pressure of the solution at the temperature of deaeration. The vapor pressure of water at 25°C is 24 mm. The indicator may also be deaerated by vigorously boiling for 15 minutes at atmospheric pressure but then must be cooled to room temperature before using.

Heat the sample to 80°C and deaerate in a 250 ml filter flask at a pressure of 2 mm of mercury until no more gas bubbles are seen but for at least two minutes. The sample must be maintained in a completely liquid state and agitated vigorously during deaeration. Even slight crystallization causes the occlusion of air. The indicator and sample should be used as soon as possible after deaeration. Transfer 2 ml of the indicator solution with a pipet into the bulb of the dilatometer. Lubricate the stopper lightly with silicone (high vacuum) grease and weigh the assembled dilatometer to the nearest 0.01 g.

Carefully overlay the indicator with the sample and fill until the sample overflows. Insert the stopper so that the indicator solution rises to approximately the 1200 mark of the stem when the stopper is securely sealed. The reading should be  $1200 \pm 100$  at 60°C if not the determination should be started over.

Remove the fat from the outer surface of the dilatometer by washing with petroleum ether. Attach the returning springs and reweigh the dilatometer when the solvent has evaporated.

Immerse the dilatometer to the 300 mark in the 60°C bath. Observe and record the upper indicator level after 15 minutes and then at 5 minute intervals until the change is less than 2 units in 5 minutes. A 60°C reading made at the end of the determination should agree with this reading. Significant variations indicate faulty technique.

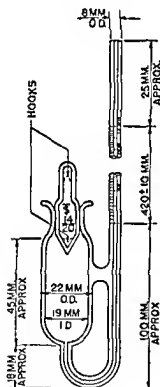


FIG. 33.6 Dilatometer  
Volumetric Type

Transfer the dilatometer to the 37.8°C. bath and immerse to the 300 mark. Read the indicator level at intervals of 5 minutes until the change is less than 2 units in 5 minutes. It is necessary that the sample be completely melted at the lower temperature. If any crystallization or clouding occurs, remelt the sample in the 60°C. bath and increase the temperature of the other bath. If the bath temperature is changed, appropriate substitutions must be made in the calculations.

Transfer the dilatometer to the 0°C. bath. Immerse to the 300 mark and hold for 15 minutes. Place in the 26.7°C. bath for 30 minutes and then transfer back to 0°C. bath and hold for 15 minutes. Place in the 26.7°C. bath for 30 minutes and then transfer back to 0°C. bath and hold for 15 minutes.

Measurement of Dilation.—Transfer the dilatometer from the 0°C. bath to a bath at the lowest desired temperature. In the case of the A.O.C.S. method 10°C. is suggested. Immerse to the 300 mark, and record reading at 30 minutes.

Repeat at the next highest temperature and so on until readings have been obtained at all of the desired temperatures.

Calculations.—

Solid fat index at temperature  $T$

$$= (\text{Total dilation}) - [(\text{Thermal expansion}) \times (60 - T)]$$

Thermal expansion of sample per degree C. in ml./kg.

$$= R(60) - R(37.8) - V_c(37.8)/W \times (60 - 37.8)$$

$$\text{Total dilation between } T \text{ and } 60^\circ\text{C. in ml./kg.} = R(60) - R(T) - V_c(T)/W$$

where  $T$  = observed temperature,

$V_c(T)$  = volume correction from Table 33-9 for expansion of glass and water at  $T$ ,

$R(T)$  = observed dilatometer reading at  $T$ , and

$W$  = weight of sample.

TABLE 33-9. VOLUME CORRECTIONS FOR GLASS AND CONFINING LIQUID

Bath Temp.	60°C. Reading				
	1000	1100	1200	1300	1400
0°C.	22.0	20.3	18.6	16.9	15.2
5	22.2	20.5	18.7	17.0	15.3
10	21.8	20.1	18.4	16.7	15.1
15	21.0	19.5	17.8	16.2	14.6
20	19.8	18.4	16.8	15.3	13.8
25	18.4	17.0	15.6	14.1	12.7
30	16.6	15.3	14.0	12.7	11.4
35	14.4	13.3	12.2	11.1	10.0
40	12.0	11.0	10.2	9.2	8.3
45	9.4	8.7	8.0	7.2	6.5
50	6.6	6.1	5.6	5.1	4.5
55	3.2	3.0	2.8	2.5	2.3
60	0	0	0	0	0



## CONSISTENCY

Consistency is defined in this instance as resistance to penetration under standardized conditions. The attainment of uniform consistency in plastic fats depends upon the establishment of equilibrium between the liquid and solid fractions and upon the cessation of crystal growth. Therefore a tempering period must be allowed the length of which may vary with the size of the package containing the fat, the character of the fat, and the temperature at which tempering is carried out. Usually 48 to 96 hours are necessary. In the standard method of the American Oil Chemists Society 48 hours at 80°C is suggested as minimal. Should there be a change in the temperature of the product after tempering an additional

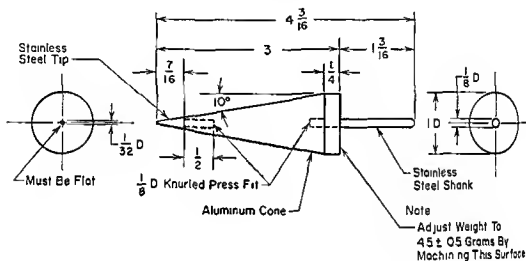


FIG. 33.7 Penetration Cone for Consistency Test

period of about 48 hours is required for reconditioning and for the establishment of new equilibrium conditions.

The penetrometer conforms to ASTM Designation D5, D217 and D937. It is essential to be able to read the depth of penetration in 0.1 mm units. The penetrating cone must be constructed of aluminum and according to the dimensions given in Fig. 33.7.

**Procedure**—Make certain the platform of the penetrometer and the cone are clean and that the latter drops freely when released. In the case of small packages of fat these may be tested without removal from the container. For large packages remove a portion of the conditioned sample from the container in the form of a cylinder or cube of convenient size. Place the fat on the platform of the penetrometer in such a position that the penetrating cone will contact the fat at least one inch from the edge of the sample. The test should be applied to the uncut and undisturbed surface of the sample. It is important to remember that any working of the portion to which the test is to be applied will lower the indicated consistency.

Lower the entire head of the penetrometer so that the tip of the cone just touches the sample. Release the cone and allow it to descend for exactly 5 seconds. The length of time the cone is allowed to travel freely in the sample is critical and must be observed with a stop watch. Immediately, lower the indicator rack which

causes the dial pointer to turn and then observe the reading on the dial. Additional tests made on the same sample must be at least 1 inch apart and the cone must be cleaned preceding each penetration. Determine the temperature of the sample and report the penetration in tenths of millimeters at the temperature of measurement.

### SPECIFIC GRAVITY<sup>1</sup>

The procedure for natural fats and oils utilizes conventional pycnometers or specific gravity bottles.

*Procedure for Natural Oils at 25°/25°C.*—Determine the weight of the water content of the pycnometer or specific gravity bottle to be used for measuring the specific gravity of fats or oils. This is done by weighing the bottle empty and after filling with distilled water.

Melt the sample and filter it through filter paper to remove any impurities and moisture that may be present. Cool the sample to 20°–23°C. and fill the bottle to overflowing, holding the bottle at an angle in such a manner as to prevent the entrapment of air bubbles as the sample is being added. Insert the stopper in the bottle and immerse and hold it in a water bath at  $25^{\circ} \pm 0.2^{\circ}\text{C.}$  for 30 minutes. Carefully wipe off any oil which has come through the capillary opening and then remove the bottle from the bath. Clean and dry it thoroughly. Weigh the bottle and contents, and calculate the specific gravity of the sample.

$$\text{Specific gravity at } 25^{\circ}/25^{\circ}\text{C.} = \frac{\text{Wt. of bottle and oil} - \text{wt. of bottle}}{\text{Wt. of water at } 25^{\circ}\text{C.}}$$

*Procedure for Natural Oils or Liquid Fats at 60°/25°C.*—The procedure is the same as described above except that the melted fat is poured into the specific gravity bottle at 56° to 58°C., and the bottle and contents are held at  $60^{\circ} \pm 0.2^{\circ}\text{C.}$  for 30 minutes before drying and weighing. Weigh the bottle and contents after they have cooled to room temperature and calculate the specific gravity of the sample. In this case, make a correction for the expansion of glass which is about 0.000025/degree.

$$\text{Specific gravity at } 60^{\circ}/25^{\circ}\text{C.} = F/W[1 + (0.000025 \times 35)]$$

where  $F$  = weight of sample at 60°C., and

$W$  = weight of water at 25°C.

*Procedure for Natural and Synthetic Drying Oils.*—In the case of natural and synthetic drying oils, Table 33-10 indicates the variations in procedure from that described above.

### VISCOSITY

The viscosity of natural fats and oils may be determined by the conventional Saybolt method. For drying oils, natural and synthetic, an adaptation of the Gardner-Holdt<sup>1</sup> bubble time procedure is standard. The Saybolt procedure is given here:

*Procedure.*—The standard orifice is satisfactory for oils having an efflux time of more than 25 seconds. Heat the sample to not more than 3°F. above the temperature at which the viscosity is to be determined. Temperatures of 100°F. and 212°F.

TABLE 33 10

<i>Viscosity of Sample (Stokes)</i>	<i>Sp Gr Bottle (type)</i>	<i>Cool to °C</i>	<i>Deter- mine at °C</i>	<i>Procedure</i>
Up to 500	Leach	20-23	25	As described above
500-2500	Hubbard	20-23	25	Centrifuge 5-15 min at 1000 r p m to remove entrapped air, then as above
Above 2500	Hubbard	20-22	25	Use 10-15 g. Remove entrapped air as before. Fill bottle with boiled and cooled distilled water. Determine wt of mixture

Specific gravity at 25°/25°C for samples having viscosities above 2500 Stokes -

$$\frac{C - A}{(B - A) \times (D - C)}$$

where *A* = Weight of empty specific gravity bottle,

*B* = Weight of specific gravity bottle plus water,

*C* = Weight of specific gravity bottle plus sample, and

*D* = Weight of specific gravity bottle plus sample plus water

are ordinarily employed. Fill the oil tube until the sample overflows and then stir the oil until the temperature is constant at the selected temperature. Quickly remove the excess oil from the gallery with a withdrawal tube. Place a receiving flask under the oil tube, withdraw the cork stopper, and at the same instant start a timer. Stop the timer when the bottom of the meniscus of the oil in the flask reaches the etched mark on the neck of the receiving flask. The efflux time in seconds is the Saybolt universal viscosity at the temperature selected for the determination.

### COOLING CURVE<sup>5</sup>

Cooling curves are used in studies of polymorphism of fats as a means of detecting phase transformation. The procedure is employed occasionally for control purposes; however, the poor conductivity of natural fats tends to cause the results to be rather indistinctive.

*Procedure*—Heat 100 g of dry sample to 65°C in a 180 ml electrolytic beaker. Place the beaker in a water bath and cool with stirring to a few degrees (5°-10°C) above the cloud point. Discontinue stirring and transfer the beaker to a water-cooled air bath maintained at a designated and constant temperature. Fix a thermometer with the bulb in the center of the sample and allow the fat to continue cooling without being disturbed, taking temperature readings every minute. Finally, plot the temperature readings versus time to obtain the cooling curve. A very important factor in determining the rate of cooling and therefore the shape of the cooling curve is the temperature differential between the sample and the cooling bath. If the rate is too rapid, some of the hesitation points may be obscured.

DIFFERENTIAL COOLING CURVE <sup>23</sup>

The differential cooling curve technique is based on the difference between the cooling rate of a reference oil (winterized cottonseed oil) which does not crystallize when cooled to 0°C. and the cooling rate of the sample which does crystallize at that temperature.

The temperature differential between the sample and the standard is measured with two copper constantin thermocouples. The constantin leads are connected together (series opposed) and the copper leads are connected to a recording potentiometer with a 0 to 1 mv. range. When connected in this manner the thermocouples measure the difference in temperature directly.

*Procedure.*—Fill two 15 x 125 mm. test tubes to a depth of 6 cm., one with the reference oil and the other with the sample. Insert the thermocouples, one in the reference oil and the other in the sample. Position the ends of the thermocouples so that they are 30 mm. from the bottoms of the tubes and in the center with respect to the walls.

Place the two tubes in a boiling water bath until the contents are at equilibrium (at least 10 minutes) and then place both in an ice water bath for cooling.

The temperature differential between the two tubes during cooling is recorded by the recording potentiometer. The shape of the curve (see Fig. 33-8) is related to phase composition.

SMOKE, FLASH AND FIRE POINTS <sup>1</sup>

*Procedure for the Smoke Point.*—Fill a Cleveland open flash cup (ASTM Designation D92-23) with the oil or melted fat sample until the top of the meniscus is exactly at the filling line. Adjust the position of the apparatus in the cabinet as shown in Fig. 33-9 so that the beam of light is directed across the center of the cup. Suspend the thermometer (20° to 760°F., in 5° subdivisions; AOCS Specification H 5-40) in a vertical position in the center of the dish with the bottom of the bulb  $\frac{1}{4}$  inch from the bottom of the cup. Heat the sample rapidly to within about 75°F. of the smoke point. Thereafter, regulate the heat so that the temperature of the sample increases at the rate of 9° to 11°F. per minute. The smoke point is the temperature indicated by the thermometer when the sample gives off a thin but continuous stream of bluish smoke. In some cases, a slight puff appears before smoke is evolved continuously. This is disregarded.

*Procedure for Oils and Fats That Flash at 300°F. and Above.*—The flash and fire points may be conducted without the cabinet but in a room or compartment free from air drafts and darkened sufficiently so that the flash is readily discernible. Avoid breathing over the surface of the sample. Fill the cup with the oil or melted fat sample so that the top of the meniscus is exactly at the filling line. Suspend or secure the thermometer in a vertical position with the bottom of the bulb  $\frac{1}{4}$  inch from the bottom of the cup and in a position half-way between the center and back of the cup. Heat the sample at a rate not to exceed 30°F. rise per minute to within 100°F. of the flash point. Thereafter regulate the rate of heating so that the temperature of the sample increases 9° to 11°F. per minute. Apply a test flame which is about  $\frac{1}{8}$  inch in diameter as the temperature reaches

<sup>23</sup> Jacobson, G. A., Tiemstra, P. J., and Pohle, W. D., J. Am. Oil Chemists' Soc., 38, 399, 1961.

each successive 5°F mark. Pass the flame in a straight line or on the circumference of a circle having a radius of at least 6 inches across the center of the cup and at right angles to the diameter passing through the thermometer. The test flame shall while passing across the surface of the sample be in the plane of the upper edge of the cup. The time for the passage of the test flame across the cup shall be about 1 second. The flash point is the temperature indicated by the ther-

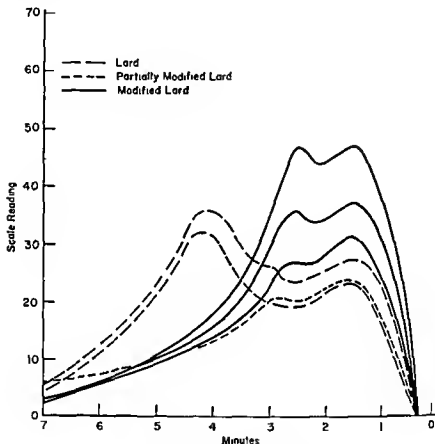


FIG 33 8 Differential Curves

monometer when a flash appears at any point on the surface of the sample. The true flash must not be confused with a bluish halo that sometimes surrounds the test flame.

**Procedure for the Fire Point**—Continue the heating after the flash point determination in the manner prescribed for the flash point until the fire point is reached. The fire point is the temperature indicated by the thermometer when application of the test flame causes burning for a period of at least five seconds.

**Procedure for Oils and Fats That Flash Below 300°F**—Oils and fats which have flash points below 300°F are tested in a Pensky Martins closed cup in which the vapors are accumulated to a concentration sufficient for their ignition. To a adequately weighed amount of the oil to be examined add 5% anhydrous cupric

sulfate. Agitate the mixture vigorously for 1 minute in a closed container and allow it to stand for 0.5 hour. Centrifuge the mixture until a sufficient amount of clear oil is obtained to make the flash point determination. Fill the cup with the sample so that the top of the meniscus is exactly at the filling line; place the lid on the cup, and adjust the apparatus for operation. Insert a flash point thermometer (AOCS Specification H 10-55) and suspend it so that the bottom of the

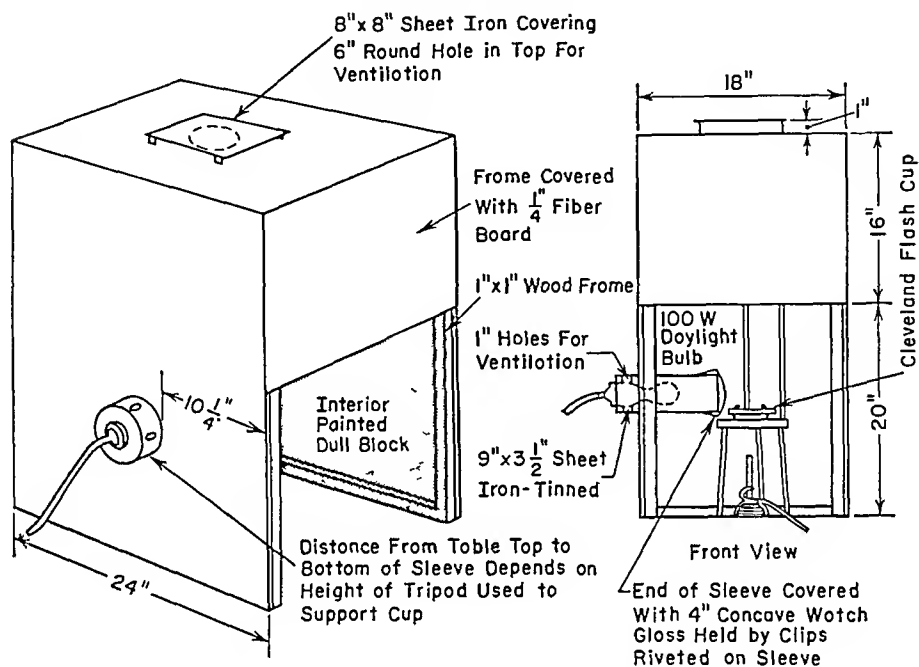


FIG. 33-9. Cabinet for Smoke Point Determination.

bulb is exactly  $1\frac{3}{4}$  inches below the level of the rim of the cup, which corresponds to the level of the lower surface of the portion of the lid inside the rim. Light the test flame and adjust so that it is the size of a bead  $\frac{5}{32}$  inch in diameter. Heat the sample so that the temperature increases not less than  $9^{\circ}\text{F.}$  nor more than  $11^{\circ}\text{F.}$  per minute. During heating, turn the stirring device from 1 to 2 revolutions per second. At every interval of  $10^{\circ}\text{F.}$  in temperature, discontinue stirring and apply the test flame by operating the device which controls the shutter and lowers the test flame into the shutter opening. Lower the test flame in 0.5 second and leave in a lowered position, for 1 second, then quickly return to the raised or high position. As soon as the test flame has been returned to the high position, resume stirring. The flash point is the temperature indicated on the thermometer at the time of the flame application that causes a distinct flash in the interior of the cup. The true flash must not be confused with the bluish halo that sometimes surrounds the test flame.

## COLOR

WESSON METHOD<sup>1</sup>

The estimation of color by the Wesson method requires a Wesson Oil Colorimeter (Greiner or Lovibond) which is standardized by the American Oil Chemists Society as described here (The Lovibond Tintometer, Model D, was recently approved by the AOCS)

The instrument consists of a light proof box with a dull black interior. The colorimeter is illuminated by a 100-watt blue frosted Mazda electric light bulb. The colorimeter is maintained in a booth or cabinet, not less than 40 inches wide and 30 inches deep. The booth or cabinet is closed so that no external light can enter. The inside of the booth is painted a dull neutral grey of Munsell value 4. The booth is illuminated by a 15 watt daylight bulb mounted 48 inches above the colorimeter box in an indirect fixture so that no direct rays strike the colorimeter or the eye of the color reader. The level of illumination in the booth at the top of the box of the colorimeter is to be not less than 1 nor more than 5 foot candles.

A block of magnesia  $1 \times 2\frac{1}{4} \times 3\frac{3}{4}$  inches is placed in the designated location and at the proper angle to reflect the light from the electric bulb vertically upward through the color tube and color glasses.

The eyepiece is finished with a dull black interior and fits over (outside of) the rectangular top of the tube holder so that the light passes through the color tube and color glasses. Eyepieces with split fields are not permitted for official trading transactions in vegetable oils but nevertheless do enable more precise readings in color ranges below about 20 red.

The tube holder (1 inch ID) is fitted with  $\frac{1}{8}$  inch ID rings at the bottom. One ring is to retain the color tube containing the oil sample and the other is to permit an equal amount of light to reach the color glasses.

Lovibond color glasses of the following designations are also required:

Red	01	02	03	04	05	06	07	08	09
	10	20	25	30	35	40	50	60	70
	76	80	90	100	110	120	160	200	
Yellow	10	20	30	50	100	150	200	350	500

Blue As may be required for certain fats, notably lard.

The red glasses must be standardized by the U. S. Bureau of Standards (Washington, D. C.) or adjusted by the Electrical Testing Laboratories (East End Ave and 79th St., New York, N. Y.). Color glasses above 10 red need not have the identical value as indicated on each glass but the exact value of each glass must be known. Keep the color glasses clean and free from oil film. Handle them carefully and protect them from acquiring scratches. It is especially important that every color glass be clean at the time of use.

The color is measured in color tubes of clear, colorless glass with a smooth flat polished bottom and of the following dimensions: length 154 mm overall inside diameter, 19 mm outside diameter, 22 mm. The color tubes are provided with two etched marks, one to indicate an oil column of 133.35 mm (5.25 inches) and another to indicate an oil column of 25.4 mm (1 inch).

**Procedure**—Make certain that the sample is clear and free from suspended matter before determining the color because suspended material, even if of colloidal

dimensions, will cause light scattering. If filtration through paper (Eaton & Dikeman No. 512, Whatman No. 12, Reeve-Angel No. 871, or S & S No. 596) does not clarify the sample completely, add diatomaceous earth (0.5 gm./300 gm. of sample) and mix together at 250 r.p.m. for 2-5 minutes at room temperature or at not more than 10°-15°C. above the melting point of the fat. Filter again through one of the designated papers.

Adjust the temperature of the sample to 25°-35°C. and fill a color tube to the etched mark. If the sample is not completely liquid at 25°-35°C., heat to a temperature of not more than 10°C. above the temperature of complete melting.

Place the tube containing the sample in the colorimeter and place alongside it such red and yellow glasses as are necessary to match the brightness of the oil, observing the colors of the oil and glasses through the eyepiece. Refer to Table 33-11 to determine the ratio of yellow glasses to red glasses that are to be used for various fats and oils. Some oils, especially soybean, are at times subject to abnormalities in the composition of their pigment content. This results in the occurrence of hues which cannot be matched, even approximately, using the fixed yellow or yellow to red ratio designated. If the indicated ratios fail to give a satisfactory match, make a second reading using the amount of yellow color required for a good match or the best possible match, and so note on the report.

If the color of the oil or fat sample exceeds 40.0 red when using the regular 133.35-mm. column, fill another tube to the 25.4-mm. mark and read the color under the same conditions as described for the longer column. It is assumed that any color result in which the column height is not designated has been read on a 133.35-mm. column.

#### *FAC COLOR STANDARDS*<sup>1</sup>

The FAC Color Standards are a series of colored liquids of varying hues designed for grading the color of inedible animal fats.

The set consists of 26 color standards, numbered with odd numbers from 1 to 45, and divided into five series. Numbers 1 to 9, inclusive, for light-colored fats; numbers 11, 11A, 11B, and 11C for very yellow fats; numbers 13 to 19, inclusive, for comparatively dark fats of a reddish cast; numbers 21 to 29, inclusive, for fats with a greenish cast; numbers 31 to 45, inclusive, for very dark fats. For the relationship between the standards see Table 33-12.

FAC Color Standards should be kept in a cool, dark area when not in use to prevent change in the color of the standards. The sample is placed in clear glass tubes of the following dimensions for viewing: 10.5 mm.  $\pm$  0.25 mm. I.D.; 12.25 mm.  $\pm$  0.25 mm. O.D.; 100 mm. long.

*Procedure.*—The sample must be entirely liquid, but it should not be heated any more than is necessary to allow filtering. At the time of reading the temperature shall not be more than 10°C. above the melting point. Filter the sample through filter paper (Eaton Dykeman No. 617 or Reeve-Angel No. 230), never using more than two papers. Pour the melted and filtered sample into a color tube. Compare the color of the sample with the color of the standards viewing the sample and standards simultaneously, preferably against a north light background. The sample shall be reported as not darker than the standard which it matches or not darker than the darker of the two standards between which it falls. Any sample darker than 45 is reported as darker than 45.



TABLE 33-11 RATIO OF YELLOW/RED GLASSES USED IN WESSON METHOD

The following ratios of yellow glasses to red glasses are to be used in determining color by the Wesson Method, except where certain trading rules specify the yellow and/or red glasses to be used in determining given grades of oil

<i>Type of oil or fat</i>	<i>Use yellow and red glass as listed below</i>
Crude coconut type	6 yellow to 1 red, up to 3 9 red 25 yellow for 4 0 to 4 9 red 30 yellow for 5 0 to 5 9 red 35 yellow for 6 0 to 6 9 red 40 yellow for 7 0 to 7 9 red 50 yellow for 8 0 to 10 9 red 70 yellow for 11 0 to 14 9 red 100 yellow for 15 0 to 19 9 red 150 yellow for 20 0 red or above
Raw inedible oils	
Tallow, greases, fatty acids	10 yellow to 1 red, up to 3 5 red 35 yellow for 3 5 to 5 0 red, incl 70 yellow for above 5 0 red
Refined oil	Use only 1 yellow glass 35 yellow for refined cotton seed oil and refined peanut oil 70 yellow for refined soybean oil Use not more than 2 red glasses up to and including 13 0 red and not more than 3 red glasses above 13 0 red
Refined and bleached oils	
Cottonseed, peanut and corn oils	10 yellow to 1 red, up to 3 5 red 35 yellow for 3 5 red or above
Coconut and palm kernel oils	6 yellow to 1 red, up to 3 9 red 10 yellow to 1 red for 3 9 red or above
Soybean oil	10 yellow to 1 red, up to 3 5 red 70 yellow for 3 5 red or above
Tallow, greases, fatty acids, etc	10 yellow to 1 red, up to 3 5 red 35 yellow for 3 5 red to 5 0 red, incl 70 yellow for above 5 0 red

## COMPOSITION OF FATS

### VOLATILE FATTY ACIDS

The Reichert Meissl and Polenske Values are used to measure volatile fatty acids which occur primarily in milk fats and lauric acid oils. The Reichert Meissl and Polenske methods presented here are standard in most areas in which such analyses are made. However these methods are highly empirical probably more so than any other procedures used in the analyses of fats and oils. No deviation

TABLE 33-12. VISUAL RELATIONSHIP IN INTENSITY BETWEEN THE FAC COLOR STANDARDS

FAC	<i>Tubes listed below are equal to or lighter than the corresponding tube in the left-hand column</i>
1	1
3	1, 3
5	1, 3, 5
7	1, 3, 5, 7
9	1, 3, 5, 7, 9
11	1, 3, 5, 7, 9, 11
11A	1, 3, 5, 7, 9, 11, 13, 11A
11B	1, 3, 5, 7, 9, 11, 13, 15, 11A, 11B
11C	1, 3, 5, 7, 9, 11, 13, 15, 17, 19, 11A, 11B, 11C
13	1, 3, 5, 7, 9, 11, 13, 11A
15	1, 3, 5, 7, 9, 11, 13, 15, 11A, 11B
17	1, 3, 5, 7, 9, 11, 13, 15, 17, 11A, 11B
19	1, 3, 5, 7, 9, 11, 13, 15, 17, 19, 11A, 11B, 11C
21	1, 3, 5, 7, 9, 11, 13, 15, 17, 19, 21, 31, 33, 11A, 11B, 11C
23	1, 3, 5, 7, 9, 11, 13, 15, 17, 19, 21, 23, 31, 33, 35, 11A, 11B, 11C
25	1, 3, 5, 7, 9, 11, 13, 15, 17, 19, 21, 23, 25, 31, 33, 35, 37, 11A, 11B, 11C
27	1, 3, 5, 7, 9, 11, 13, 15, 17, 19, 21, 23, 25, 27, 31, 33, 35, 37, 39, 11A, 11B, 11C
29	1, 3, 5, 7, 9, 11, 13, 15, 17, 19, 21, 23, 25, 27, 29, 31, 33, 35, 37, 39, 41, 43, 11A, 11B, 11C
31	1, 3, 5, 7, 9, 11, 13, 15, 17, 19, 31, 11A, 11B, 11C
33	1, 3, 5, 7, 9, 11, 13, 15, 17, 19, 21, 31, 33, 11A, 11B, 11C
35	1, 3, 5, 7, 9, 11, 13, 15, 17, 19, 21, 23, 31, 33, 35, 11A, 11B, 11C
37	1, 3, 5, 7, 9, 11, 13, 15, 17, 19, 21, 23, 25, 31, 33, 35, 37, 11A, 11B, 11C
39	1, 3, 5, 7, 9, 11, 13, 15, 17, 19, 21, 23, 25, 27, 31, 33, 35, 37, 39, 11A, 11B, 11C
41	1, 3, 5, 7, 9, 11, 13, 15, 17, 19, 21, 23, 25, 27, 31, 33, 35, 37, 39, 41, 11A, 11B, 11C
43	1, 3, 5, 7, 9, 11, 13, 15, 17, 19, 21, 23, 25, 27, 29, 31, 33, 35, 37, 39, 41, 43, 11A, 11B, 11C
45	1, 3, 5, 7, 9, 11, 13, 15, 17, 19, 21, 23, 25, 27, 29, 31, 33, 35, 37, 39, 41, 43, 45, 11A, 11B, 11C

is allowable in either application or technique if results are to be meaningful. Chromatographic methods, recently developed, provide more accurate means of determining the individual fatty acids.

The Reichert-Meissl Value is a measure of volatile fatty acids (chiefly butyric and caproic) and the Polenske Value is an index of the insoluble volatile fatty acids (caprylic, capric, and lauric).

#### REICHERT-MEISSL VALUE

**Procedure.**<sup>1</sup>—Filter the oil or melted fat through filter paper to remove moisture and impurities. Weigh 5.0 g. of sample into the distillation flask (see Fig. 33-10). Add 20 ml. of a mixture of glycerol and 50% sodium hydroxide solution (180 + 20, v/v) and heat until the fat is completely saponified. The solution should be

clear. Add 135 ml of recently boiled distilled water, drop by drop at first to avoid foaming and then add 6 ml of dilute sulfuric acid (20%, v/v) and a few pieces of pumice stone.

Distill without previously melting the fatty acids at such a rate that 110 ml are collected in as nearly 30 minutes as possible. The temperature of the distillate entering the receiving flask must not exceed 20°C. When exactly 110 ml of distillate have been collected, discontinue heating and replace the receiver by a 25 ml cylinder.

Mix the contents of the recovery flask gently and then immerse in a water bath at 15°C for 15 minutes. Filter the distillate through filter paper and titrate 100 ml of the distillate with 0.1 N sodium hydroxide solution using 0.5 ml of phenolphthalein (1% in 95% alcohol) to the appearance of a pink color which persists for 2-3 minutes.

Prepare and conduct a blank determination similar in all respects except for omission of the sample.

The Reichert Meissl Value 11X (titration of sample - titration of blank)

#### POLENSEK VALUE

**Procedure.**<sup>1</sup>—Wash the residue on the filter paper with three 15 ml portions of distilled water, each having been previously passed through the condenser, the 25 ml cylinder and the 110 ml receiving flask. Discard these

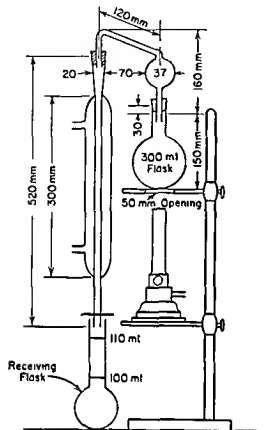


Fig. 33-10 Reichert Meissl Polenske Distillation Apparatus

water washings. Wash the residue on the filter paper again to dissolve the insoluble acids this time using three 15 ml portions of 95% alcohol which have been previously neutralized. Titrate the alcohol solution with 0.1 N sodium hydroxide using 0.5 ml of phenolphthalein to the appearance of a pink color which will persist for 2 to 3 minutes. Conduct a blank determination similar in all respects except that the sample is omitted.

The Polenske Value = titration of sample - titration of blank.

#### BUTYRIC ACID<sup>24</sup>

The reagents required for the chromatographic determination of butyric acid include

**Reagents.** Silicic Acid—Heat the acid in a shallow pan or evaporating dish for 18 hours at 175°C and store it in a desiccator or in a tightly sealed container.

<sup>24</sup> Anglin, C. and Mahon, J. H. J. Assoc. Off. Agr. Chemists 39, 365, 1956.

**Bromocresol Green-Glycol Solution.**—Dissolve 700 mg. of bromocresol green in 700 ml. of ethylene glycol by warming on steam bath. Cool and then add about 200 ml. of water. Prepare 0.1 *N* ammonium hydroxide by diluting about 6.6 ml. of ammonium hydroxide (sp. gr. 0.90) to 1 liter with water. Add 40 ml. of this solution to the indicator solution and then add additional water to make 1 liter. Store this ink-blue solution in a glass-stoppered bottle.

**Packing Material.**—Mix 100 g. of silicic acid with about 95 ml. of bromocresol green-glycol solution until a homogeneous olive-green powder is obtained. The mixing may be done in small batches in a mortar or in larger batches in a mechanical mixer. Prepared packing material may be stored in a tightly stoppered container for several months.

**Hexane-Butanol Mixture.**—Add one volume of *n*-butanol to 100 volumes of *n*-hexane.

**Isopropanol-KOH Solution.**—Dissolve 25 g. of potassium hydroxide pellets in 400 ml. of isopropanol by warming and swirling on a steam bath. Cool and decant the supernatant isopropanol-potassium hydroxide solution, which should contain about 50 mg. of KOH/ml. Store in a refrigerator.

**Potassium Hydroxide Solution, Approximately 0.05 *N*.**—Dilute 60 ml. of the isopropanol-KOH solution with 440 ml. of isopropanol and 500 ml. of methanol. Store in an amber bottle.

**Thymol Blue Solution.**—Dissolve 300 mg. of thymol blue in 25 ml. of 0.05 *N* alcoholic potassium hydroxide solution and add 75 ml. of isopropanol.

**Procedure.** Preparation of the Sample.—Place 0.5–0.7 g. of well mixed, melted fat in a 20 × 150-mm. test tube. Add 5 ml. of isopropanol-potassium hydroxide solution and some boiling chips. Place the tube in a boiling water bath to saponify the fat and evaporate the isopropanol, leaving the solid soap.

Determine the amount of dilute sulfuric acid (2 + 1, v/v) equivalent to 5 ml. of isopropanol-potassium hydroxide solution in 10 ml. of water containing 2 drops of thymol blue solution by placing these in a small beaker or flask and adding dilute sulfuric acid dropwise until the color becomes red.

Place the test tube containing the saponified fat in a cold water bath and add the indicated quantity of dilute sulfuric acid. Break up the lumps in the bottom of the tube with a glass stirring rod. After thoroughly mixing the mass in the test tube, a yellow mixture of fatty acids clinging to a viscous aqueous layer of potassium sulfate should result. Add ten ml. of the hexane-butanol solution and again mix thoroughly with the glass rod. The aqueous phase should now cling to the precipitate of potassium hydroxide allowing easy separation. Decant the hexane-butanol solution of fatty acids which is ready to be chromatographed.

The top of the chromatographic column should be yellow. If the top of the chromatographic column turns blue on the addition of the fatty acid solution, the need of more sulfuric acid is indicated.

**Preparation of the Column.**—Prepare a chromatographic column by fusing a 15-cm. section of glass tubing (38 mm. O.D.) to a 20-cm. section of glass tubing (22 mm. O.D.) and this in turn is fused to a 5-cm. length of 7-mm. tubing with a drawn out tip. Overlay 35 g. of packing material with the hexane-butanol mixture in a mortar and mix with a pestle to form a slurry. Place a small glass wool plug loosely in the constricted end of the column and gently tamp it into place with a glass rod. Place a finger over the constricted end of the column and add the hexane-butanol mixture until the reservoir is half full. With the aid of a teaspoon, underlay the prepared slurry beneath the solvent. Move the spoon up and down

## MONOGLYCERIDES

The mono- and diglycerides are fatty compounds in which two, or one respectively, of the fatty acid radicals of the triglyceride molecule are replaced by hydroxyl groups. Commercial monoglycerides containing both isomers are used extensively for fat emulsification purposes. There is no standard method for the estimation of diglycerides but they have been determined chromatographically.

PERIODIC ACID METHOD <sup>25</sup>

Prepare the periodic acid solution by dissolving 5.4 g. of periodic acid (reagent grade) in 100 ml. of distilled water and adding 1900 ml. of glacial acetic acid. Protect this solution from light during storage.

The suitability of this reagent for the estimation of monoglyceride is determined by the following test: To 0.5–0.6 g. of pure glycerol dissolved in 50 ml. of distilled water, add 50 ml. of the periodic acid solution. Prepare a blank by adding 50 ml. of periodic acid to 50 ml. of distilled water. Allow the solution and blank to stand for 30 minutes and then titrate them as described later for the estimation of monoglyceride. The titration of the solution containing the glycerol divided by the titration of the blank should be between 0.75 and 0.76; if not, the periodic acid is unsatisfactory.

Evaluate the suitability of the chloroform by titrating two 50-ml. portions of periodic acid solution, one containing 50 ml. of chloroform and the other containing 50 ml. of water. These titrations should differ by no more than 0.5 ml.

**Preparation of Sample.**—The samples should be homogeneous. If melting is necessary, the temperature during melting should not exceed 10°C. above the melting point of the fat. Excessive heating may lead to a reduction in the monoglyceride content of the sample. Some commercially produced monoglycerides contain free glycerol. In such instances, withdraw the portion to be weighed and analyzed while the sample is completely liquid and under vigorous agitation.

**Procedure for Alpha-Monoglycerides.**—Weigh accurately the size of sample indicated in Table 33-13 depending upon the monoglyceride content.

TABLE 33-13. SIZE OF SAMPLE REQUIRED FOR DETERMINATION OF MONOGLYCERIDE

<i>Monoglyceride, %</i>	<i>Size of Sample, in g.</i>
100	0.30 ± 0.0002
75	0.40 ± 0.0002
50	0.60 ± 0.0003
40	0.70 ± 0.0005
30	1.00 ± 0.001
20	1.50 ± 0.001
10	3.00 ± 0.002
5	6.00 ± 0.004
3 or less	10.00 ± 0.01

Dissolve the sample in chloroform and transfer the solution to a 100-ml. glass-stoppered volumetric flask with small portions of chloroform. Add sufficient chloroform to the flask to bring the total volume to 100 ml. Pour the entire contents of the volumetric flask into a 500-ml. glass-stoppered Erlenmeyer flask and add

<sup>25</sup> Pohle, W. D., and Mehlenbacher, V. C., J. Am. Oil Chemists' Soc., 27, 51, 1950.

100 ml of distilled water. If emulsions form which will not separate use 100 ml of 5% acetic acid instead of distilled water. Stopper the flask and shake the contents vigorously for 1 minute and then allow the mixture to stand until the aqueous phase separates from the chloroform layer. This usually requires from 1 to 3 hours. After separation the chloroform layer should be clear or at most only slightly cloudy. Pipet 50 ml of periodic acid reagent into a 400 ml beaker and add 50 ml of the chloroform solution of the sample. Prepare and conduct blank determinations similar to the sample in all respects but using 50 ml of chloroform instead of the sample solution. Swirl the beakers gently to mix.

Cover the beakers with watch glasses and allow the solutions to stand for 30 minutes. At no time allow the temperature of the sample solution or the temperature of the blank to exceed 95°F. Add 20 ml of 15% potassium iodide and swirl to mix. Allow to stand for at least 1 minute but never more than 5 minutes before titrating and avoid strong sunlight. Add 100 ml of distilled water and then titrate with 0.1 N sodium thiosulfate solution using an electric stirrer to keep the solution thoroughly mixed. Continue the titration to the disappearance of the brown iodine color from the aqueous layer. Add 2 ml of starch indicator (10 g/liter of water) and continue the titration to the disappearance of the blue iodostarch color from the aqueous layer. Vigorous agitation of the solution is essential for complete removal of iodine from the chloroform layer.

The correct excess of periodic acid is essential and critical. The correct excess of reagent is governed by the selection of the proper size of sample as indicated in Table 33.13 and it may be further confirmed by the following criteria. The titration of the sample should be at least 0.8 of the titration of the blank if it is not use a smaller sample. If the titration of the blank minus the titration of the sample is less than 4 ml use a larger sample but the size of the sample should never exceed 10 g.

$$\% \alpha \text{ Monoglyceride} = \frac{(B - S) \times N \times 17.927}{W}$$

where  $B$  = titration of blank

$S$  = titration of sample

$N$  = normality of sodium thiosulfate solution and

$W$  = weight of sample in aliquot

17.927 = molecular weight of monostearin 20

**Procedure for Total Monoglycerides**<sup>26</sup>—Transfer about 90 ml of the chloroform solution to a glass stoppered Erlenmeyer flask and add 0.08 ml of 56% perchloric acid. Shake the flask and contents for 1 minute and then allow to stand for 9 additional minutes. Pipet 50 ml of the periodic acid solution into a 400 ml beaker add 50 ml of the chloroform sample solution and allow to stand for 30 minutes. Determine the total monoglyceride content as previously directed for the determination of  $\alpha$  monoglyceride beginning with the addition of potassium iodide. Prepare and conduct a blank. The same precautions with regard to temperature should be practiced as before.

$$\% \text{ Total monoglyceride} = \frac{1.15 (B - S) \times N \times 17.927}{W}$$

$$\% \beta \text{ Monoglyceride} = \% \text{ total monoglyceride} - \% \alpha \text{ monoglyceride}$$

<sup>26</sup> Brokaw, G. Y., Perry, E. S., and Lyman, W. C. J. Am. Oil Chemists Soc. 32, 191 (1955)

## FREE AND COMBINED GLYCEROL IN FATS AND OILS

PERIODIC ACID METHOD<sup>1</sup>

**Reagent.**—Prepare the periodic acid reagent for the determination of glycerol by dissolving 5.4 g. of periodic acid in 100 ml. distilled water and then adding 1900 ml. of glacial acetic acid. Mix the solution thoroughly and store it in a dark, glass-stoppered bottle or keep it in a clear, glass-stoppered bottle which is maintained in a darkened area.

**Procedure for Free Glycerol.**—Weigh about  $10 \pm 0.01$  g. of the sample, wash into a 1-liter volumetric flask with  $90 \pm 0.2$  ml. of chloroform. Add approximately 500 ml. of distilled water, insert a stopper and shake the flask vigorously for 30 to 60 seconds. Add distilled water to make 1 liter, insert the stopper, and invert the flask several times to assure thorough mixing. Allow the mixture to stand until the chloroform and aqueous portions separate.

Transfer with a pipet 50 ml. of periodic acid into a 400-ml. beaker, and add 100 ml. of the aqueous portion of the sample solution (filtered if it contains suspended matter) from the 1-liter flask. Shake or swirl gently to mix. Allow to stand for 30 minutes, add 20 ml. of 15% potassium iodide, mix and then allow to stand for at least 1 but not more than 5 minutes. Avoid bright light.

Dilute the contents of the beaker to about 200 ml. and then titrate with 0.1 *N* sodium thiosulfate solution using 2 ml. of starch solution as the indicator.

Prepare and conduct a blank determination similar to the sample using 100 ml. of distilled water in place of sample. The titration of the sample (ml. of 0.1 *N*  $\text{Na}_2\text{S}_2\text{O}_3$ ) must be at least 0.8 of the titration of the blank; otherwise, there is insufficient excess of periodic acid. In this case, repeat the determination using a smaller portion of the sample.

$$\% \text{ Free glycerol} = \frac{(B - S) \times N \times 2.302}{\text{Wt. of sample in aliquot titrated}},$$

where *B* = titration of blank,

*S* = titration of sample, and

*N* = normality of sodium thiosulfate solution.

**Procedure for Total (Free and Combined) Glycerol.**—The size of sample to weigh and the amount of alkali and chloroform required are indicated in Table 33-14.

TABLE 33-14. SIZE OF SAMPLE AND QUANTITIES OF ALKALI AND CHOLOROFORM REQUIRED FOR DETERMINATION OF TOTAL GLYCEROL IN FATS

Total Glycerol	Approximate Size Sample	Alcoholic Potassium Hydroxide (40 g./liter)	Chloroform To Be Added
%	g.	ml.	ml.
10 to 40	$2 \pm 0.001$	50	$99 \pm 0.2$
5 to 20	$4 \pm 0.003$	50	$96 \pm 0.2$
2 to 8	$10 \pm 0.01$	100	$91 \pm 0.2$

Place the weighed sample and indicated alkali in an Erlenmeyer flask attach an air condenser to the flask and boil the mixture gently for 30 minutes to saponify the fat. Wash down the condenser with a little distilled water and pour the contents of the flask into a 1 liter volumetric flask to which has previously been added the indicated quantity of chloroform. Add 25 ml of glacial acetic acid to the volumetric flask. Wash the Erlenmeyer flask with three 25 ml portions of distilled water and transfer all of the washings to the volumetric flask. Add about 500 ml of distilled water to the volumetric flask stopper and shake vigorously for 30 to 60 seconds. Add distilled water to bring the volume to 1 liter. Insert the stopper and invert the flask several times to assure thorough mixing. Allow to stand until the layers separate.

The procedure from this point and the calculations are the same as previously described for free glycerol using aliquots of the aqueous portion withdrawn from the 1 liter volumetric flask. The combined glycerol equals the total glycerol minus the free glycerol.

## POLYUNSATURATED FATTY ACIDS

### ULTRAVIOLET SPECTROPHOTOMETRIC METHOD<sup>1</sup>

**Apparatus**—The apparatus required for the determination of polyunsaturated fatty acids according to the method of the American Oil Chemists' Society should comply with the following specifications:

The ultraviolet spectrophotometer should cover a spectral range of 220  $m\mu$  to 360  $m\mu$  with wavelength scale readable to 0.1  $m\mu$ . It should be provided with a compartment for holding 1 000 to 10 000 cm cells. The Beckman Model DU with hydrogen discharge lamp is satisfactory. Adjust the Beckman spectrophotometer in the following manner before using. Open the slits of the Beckman instrument to the maximum width of 20 mm and turn the sensitivity knob to the counter clockwise limit. Then adjust the focus of the hydrogen discharge lamp with no absorption cell in the beam so that the meter balances at the lowest possible wavelength (usually 211  $m\mu$  or lower). In making absorption measurements, the sensitivity control is usually set at 3 counterclockwise turns from its clockwise limit, the slit width control is usually employed as a coarse adjustment for balancing the instrument and the sensitivity control for final adjustment. In general width of the slit is critical in this method only for absorption measurements at 262, 268, and 274  $m\mu$ . When making absorption measurements on isomerized samples in this region the slit width at the final balancing adjustment must be 0.8 to 0.9 mm.

The absorption cells should be quartz with matched pairs of lengths 1 000 to 10 00  $\pm$  0.005 cm. The cells of a pair when filled with water or isooctane must match within 0.01 absorbance units. Use the nondemountable type made of quartz or the demountable type consisting of Pyrex glass cell body of outside diameter of about 22 mm with centered ground glass stopper, threaded metal caps polished crystalline quartz windows, and cork gaskets.

**Reagents**—The reagents should comply with the specifications given below or purified accordingly.

**Absolute Synthetic Methanol or Ethanol**—Check the absorbance of 1 cm layer of methanol against distilled water at 220  $m\mu$  and through the range of wavelengths employed in the analysis. The absorbance at 220  $m\mu$  compared with distilled water set at zero density must be less than 0.4 and the curve should be smooth in the range 262 to 322  $m\mu$ . If the alcohol does not comply with the foregoing



specifications, purify it according to the following procedure. Place 2000 ml. of methanol into a 3-liter distilling flask, double-neck type. Add to the flask 10 g. of potassium hydroxide (reagent grade) and 25 g. of zinc powder. Place a glass stopper in 1 outlet of the flask and a reflux tube in the other. Reflux on the steam bath for 3 hours. Remove from the steam bath and replace the reflux tube with a trap, 75° connecting tube, and condenser. Place the flask in a water bath or electric heating mantle and heat to distill the methanol. Collect the distillate in a 2-liter Erlenmeyer flask. Determine the absorbance and if it complies store in a glass-stoppered bottle for further use. . . .

Isooctane (2,2,4-trimethylpentane), spectral grade, should be purified to comply with the specific requirements for absorbance. Hexane and cyclohexane are also satisfactory providing they comply with the specification for isooctane. Place about 3½" of glass wool above the stopcock at the lower end of a 32" x 1¾" filter tube. Add about 12" of silica gel. Fasten the tube vertically to a ring stand and pour the isooctane into the tube, filling it about three-fourths full. Insert a cork stopper covered with aluminum foil loosely in the top of the tube and allow the isooctane to filter through the silica gel. Renew the silica gel in the tube as often as necessary to yield isooctane conforming to the required absorbance limits.

Check the absorbance of a 1-cm. layer of the isooctane against distilled water through the range of wavelengths used in the analysis. The absorbance compared with distilled water set at zero absorbance must not be more than 0.070 at all wavelengths and the resultant absorbance vs. wavelength curve must be smooth; otherwise, repeat the filtration and recheck the absorbance.

**Potassium Hydroxide-Glycol Solution, 6.6% KOH for 25-Minute Isomerization.**—Weigh about 750.0 g. of ethylene glycol into a 1-liter round-bottom Pyrex flask. Close with a hollow ground-glass stopper which contains a short outlet tube and an inlet tube reaching to the bottom of the flask. Connect the inlet to an oxygen-free nitrogen supply and bubble the gas through the liquid to exclude all air and to agitate the liquid slightly. Place an oil bath maintained at 100° to 150°C. around the flask. Raise the bath temperature to 190°C. and hold this temperature for 10 minutes. Lower the bath and allow the bath temperature to drop to 120°C. When the bath temperature reaches 120°C., carefully add 60 g. of potassium hydroxide (85%, A.C.S. grade pellets) to the glycol, keeping the solution under agitation with nitrogen (50 to 100 ml. per min.). Remove the bath and allow the KOH-glycol solution to cool. Remove the hollow glass stopper and close with a solid glass stopper. Store in a refrigerator at about 40°F. under nitrogen. Neutralize about 90 ml. of methanol with 1 *N* hydrochloric acid using phenolphthalein indicator. Add 10.00 g. of the KOH-glycol solution, mix thoroughly and add 0.5 ml. of phenolphthalein indicator solution. Titrate with standardized hydrochloric acid until the pink color has just disappeared.

$$\% \text{ Potassium hydroxide} = \frac{\text{titration} \times \text{normality} \times 5.61}{\text{Wt. of solution}}$$

If the alkali-glycol solution is above the designated strength of 6.5–6.6% KOH it may be adjusted by the addition of glycol, previously dried at 190°C. as already described.

Prepare the 21%-KOH solution in a similar manner but use 210 g. of 85% KOH pellets instead of 60 g. The limits for this solution are 21 ± 0.1% KOH.

**Procedure for Conjugated Polyunsaturated Acids**—Weigh accurately into a 1 ml Pyrex cup sufficient sample to give an absorbance reading of 0.2 or more. This is usually about 200 mg. Place approximately 75 ml of purified isooctane, hexane, or cyclohexane in a 150 ml beaker. Hold the cup just above the solvent and allow it to drop to the bottom of the beaker. Rotate the beaker and warm the contents if necessary to promote solution of the sample. Then cool the beaker and contents to room temperature and quantitatively transfer the solution to a 100-ml glass stoppered volumetric flask and add sufficient solvent to bring the volume to 100 ml. Mix thoroughly. Determine the absorbance of the solution in the ultra violet absorption spectrophotometer, following the manufacturer's instructions for operating the instrument. Use a matched cell containing only solvent as the blank cell.

Determine the absorbance readings at 346, 322, 315, 308, 274, 268, 262, and 233 m $\mu$ , diluting the original solution and/or using other cell lengths if necessary so that the observed densities are between 0.2 and 0.8. Record the cell length, grams of sample in a liter of the final dilution used for the measurement, and the absorbance reading for each wavelength. Readings are not necessarily required at all wavelengths for all samples. If the history of the sample is known, it is not necessary to make readings at wavelengths higher than those which correspond to the most highly unsaturated acids known to be present. It is convenient to make readings on both sides of the wavelengths indicated to ascertain that a maximum is present. A component is assumed to be absent if a maximum is not found in the characteristic region and no further calculations are made in this region.

**Procedure for Nonconjugated Polyunsaturated Acids Using 6.6% KOH and 25 Minute Isomerization**—This method is preferred where the sample contains only linoleic and linolenic unsaturated acids. Weigh about 100 mg of sample into a 1 ml Pyrex glass cup and weigh  $11.0 \pm 0.1$  g of the 6.6% KOH glycol reagent into a 250 x 25 mm test tube. Prepare and conduct 2 blanks with each group of samples. Cover the test tube with a distributing head attached to a manifold which will permit passing nitrogen (containing no more than 0.01% oxygen) over the contents of the tubes at the rate of 50–100 ml/min. Start and adjust the flow of nitrogen and allow the gas to sweep through the tube for about 1 minute to replace the air, and then immerse the tube and contents to a depth of 11.5 cm in a bath maintained at  $180.0^\circ \pm 0.5^\circ\text{C}$ . Maintenance at this temperature is important and should be checked frequently. Remove the distributing head after 20 minutes of heating and drop the 1 ml glass cup containing the weighed sample into the test tube. Observe the exact time when the cup is dropped into the tube and replace the distributing head. Conduct the KOH glycol blank in a similar manner but use a clean 1 ml glass cup and omit the sample. Keeping the distributing head in place, remove each test tube from the bath and swirl vigorously for a few seconds and then return to the bath. After heating for 1 minute, remove and examine the solution in each tube. If the solution is clear, indicating complete saponification, return the tube to the bath. If the solution is not clear, swirl the test tube two or three times and again return to the bath. Repeat the inspection after 1 minute of heating and continue the swirling, heating and inspection until saponification is complete. Exactly 25 minutes after dropping the sample into the test tube, remove the tube from the bath, wipe it clean, and place it in a 3000-ml beaker containing cold water. Continue to pass nitrogen over the solution during the cooling process. When the solution has cooled to room temperature, remove the head from the test tube and wash the lower tubing on the head with about 20

ml. of methanol, collecting the washings in the test tube. Use a long glass stirring rod to mix and quantitatively transfer the contents of the test tube to a 100-ml. glass-stoppered volumetric flask. Dilute to volume with methanol and mix thoroughly.

Determine the absorbance readings at 346, 322, 315, 308, 274, 268, 262, and 233  $m\mu$ , using dilutions such that the absorbance values will lie between 0.2 and 0.8.

**Procedure for Nonconjugated Polyunsaturated Acids Using 21% KOH-Glycol Reagent and 15-Minute Isomerization.**—This method is preferred for the analysis of samples containing linoleic, linolenic, and arachidonic acids and it is essential when linoleic, linolenic, arachidonic, and pentaenoic acids are present.

This procedure is performed as directed in the preceding method except that the reagent is 21% potassium hydroxide in ethylene glycol, the sample size is 80 mg., and the isomerization period is 15 minutes.

**Calculations. Absorptivities for Conjugated Constituents.**—Calculate the absorptivity ( $a$ ) for each wavelength, using the following equations where

$$a = \frac{A}{bc}$$

where  $A$  = observed absorbance at each wavelength,

$b$  = cell length in cm., and

$c$  = concentration in grams of sample per liter of the final dilution used for the absorbance measurements.

The subscripts <sub>2</sub>, <sub>3</sub>, <sub>4</sub>, and <sub>5</sub> used in these calculations refer to the diene, triene, tetraene, and pentaene constituents, respectively.

$$a_2 \text{ at } 233 \text{ } m\mu \text{ corrected for absorption due to acid or ester groups} = a_{233} - a_0$$

where  $a_0 = 0.07$  for esters, 0.03 for soaps and fatty acids.

$$a_3 \text{ at } 268 \text{ } m\mu \text{ corrected for background absorption} = 2.8 \left( a_{268} - \frac{a_{262} + a_{274}}{2} \right)$$

$$a_4 \text{ at } 315 \text{ } m\mu \text{ corrected for background absorption} = 2.5 \left( a_{315} - \frac{a_{308} + a_{322}}{2} \right)$$

$$a_5 \text{ at } 346 \text{ } m\mu = a_{346}$$

**Conjugated Acids.**—If the quantities within the parentheses are zero or negative, no characteristic maxima are present and the corresponding constituent is negative. Preformed constituents are usually present in small quantities so that corrections for background absorption are usually required. No background is applied to readings in the pentaenoic region; that is, at 346  $m\mu$ .

$$\% \text{ conjugated diene, } C_2 = 0.91a_2$$

$$\% \text{ conjugated triene, } C_3 = 0.47a_3$$

$$\% \text{ conjugated tetraene, } C_4 = 0.45a_4$$

$$\% \text{ conjugated pentaene, } C_5 = 0.39a_5$$

**Absorptivities for Nonconjugated Constituents Using 6.6% KOH-Glycol Reagent and 25-Minute Isomerization.**—Calculate the absorptivities ( $a'$ ) for each wavelength

using the following equations where  $a = \frac{A}{bc}$ . These equations involve the appropriate corrections at each wavelength

$$a'_2 = a'_{233} - a_2 - 0.03$$

$$a'_3 = 4.03 \left( a'_{263} - \frac{a'_{262} + a'_{274}}{2} \right) - a_3$$

$$a'_4 = 2.06 \left( a'_{315} - \frac{a'_{308} + a'_{322}}{2} \right) - a_4$$

*Nonconjugated Acids Using 6.6% KOH Glycol Reagent and 25 Minute Isomerization (Without Background Correction) —*

$$\% \text{ linoleic acid} = 1.086 a_2 - 1.324 (a'_{263} - a_{263}) + 0.040 (a'_{315} - a_{315})$$

$$\% \text{ linolenic acid} = 1.980 (a'_{268} - a_{263}) - 4.92 (a'_{315} - a_{315})$$

$$\% \text{ arachidonic acid} = 4.67 (a'_{315} - a_{315})$$

*Nonconjugated Acids (With Background Correction) —*

$$\% \text{ linoleic acid} = 1.086 a' - 1.324 a'_3 + 0.40 a'_4$$

$$\% \text{ linolenic acid} = 1.980 a'_3 - 4.92 a'_4$$

$$\% \text{ arachidonic acid} = 4.69 a'_4$$

*Absorptivities for Nonconjugated Constituents Using 21% KOH Glycol Reagent and 15 Minute Isomerization —* Calculate the absorptivity ( $a$ ) for each wavelength using the equations previously designated

$$a'_2 = a'_{223} - a_2$$

$$a'_3 = a'_{263} - a_{263}$$

$$a'_4 = a_{315} - a_{315}$$

$$a'_5 = a'_{345} - a_{345}$$

*Nonconjugated Acids Using 21% KOH Glycol Reagent and 15 Minute Isomerization —* The spectrophotometric method will not differentiate between  $C_{20}$  and  $C$  pentaenes. If chain length is unknown it is assumed that both are present in equal quantities and the third set of equations given below is used

For samples containing  $C_{20}$  pentaene acid

$$\% \text{ linoleic acid} = 1.09 a'_2 - 0.57 a'_3 - 0.26 a'_4 + 0.002 a'_5$$

$$\% \text{ linolenic acid} = 1.10 a'_3 - 0.88 a'_4 + 0.31 a'_5$$

$$\% \text{ arachidonic acid} = 1.65 a'_4 - 1.55 a'_5$$

$$\% \text{ pentaenoic acid} = 1.14 a'_5$$

For samples containing C<sub>22</sub> pentaene acid:

$$\% \text{ linoleic acid} = 1.09a'_2 - 0.57a'_3 - 0.26a'_4 - 0.12a'_5$$

$$\% \text{ linolenic acid} = 1.10a'_3 - 0.88a'_4 - 0.02a'_5$$

$$\% \text{ arachidonic acid} = 1.65a'_4 - 1.86a'_5$$

$$\% \text{ pentaenoic acid} = 1.98a'_5$$

For samples containing pentaene acids of unknown chain length:

$$\% \text{ linoleic acid} = 1.09a'_2 - 0.57a'_3 - 0.26a'_4 - 0.03a'_5$$

$$\% \text{ linolenic acid} = 1.10a'_3 - 0.88a'_4 + 0.19a'_5$$

$$\% \text{ arachidonic acid} = 1.65a'_4 - 1.67a'_5$$

$$\% \text{ pentaenoic acid} = 1.45a'_5$$

Total composition:

% Conjugated polyunsaturated fatty acid = a summation of the diene, triene, tetraene, and pentaene constituents determined.

% Nonconjugated polyunsaturated fatty acid = a summation of the dienoid, trienoid, tetraenoid, and pentaenoid acids determined.

The oleic acid content can be determined from the iodine value of the sample and the following equation:

% Oleic acid

$$= \frac{\text{I.V.} - (1.811(C_2 + X) + 2.737C_3 + Y) + 3.337(C_4 + Z) + 4.014(C_5 + P)}{0.899},$$

where C<sub>2</sub>, C<sub>3</sub>, C<sub>4</sub>, C<sub>5</sub> are conjugated diene, triene, etc. and X, Y, Z, and P are % linoleic, linolenic acids, etc.

% Saturated acids = % Total fatty acid - (% oleic acid + % conjugated acids + % nonconjugated acids);

the % total fatty acid content of most natural oils is 95.6.

## FATTY ACIDS

### GAS CHROMATOGRAPHY

The GLC procedure for analyzing fatty acids involves passing a sample of the fatty mixture to be analyzed through a heated column by means of an inert carrier gas such as nitrogen or helium. In the column is contained a stationary phase precoated over an inactive substance such as diatomaceous earth. The components of the mixture are eluted with the gas and resolved in the column. When the individual components of the mixture arrive at the exit end of the column, they are detected and measured by some suitable means.

The retention time is a measure of the time required for a given component to pass through the column. While the retention time is related to the compound

and the stationary phase it is also influenced by other factors including design of the column and the method of operation of the column

Even though a relatively new technique gas chromatography provides the best procedure available for the separation of fatty acid mixtures and for the determination of the individual constituents of such mixtures

There are available on the commercial market several instruments for performing gas chromatography which appear to yield satisfactory and comparable results. It appears that some latitude in apparatus is tolerable however it should be noted that the details of operation and method may have to be modified to correspond with any given unit

**Apparatus**—The essential features of the assembly of apparatus are these

**Column**—Glass or stainless steel  $\frac{1}{8}$  inch I.D. 6–10 feet in length but other lengths have been used. Inlet temperature must be approximately 50°C above column temperature

**Detector**—Several types are available based on conductivity, ionization density, etc. This should be maintained at the temperature of the column or at not more than 25°C above

**Recorder**—0 to 1 mv range 1 second full scale deflection with a chart speed of  $\frac{1}{2}$  inch/min. Attenuator switch to change recorder range should be provided

**Carrier Gas**—Inert gas such as nitrogen, helium or argon

**Supporting Phase**—A special grade of Celite designated as Chromasorb W is most generally used

**Stationary Phase**—Most commonly employed have been the aziepons and the polyesters of adipic or succinic acids. When the former are used the fatty acid esters exit from the column in the order of boiling point. When the polyesters are used the exit is in the order of decreasing saturation for the same number of carbon atoms. There is therefore improved resolution with the polyesters and of these the esters of succinic acid seem to be preferred

**Preparation of the Methyl Esters**—The practice is to employ the methyl esters of the fatty acids for analysis. The two methods for the preparation of the methyl esters presented here are relatively rapid and easy to perform

**Triglycerides**—Add 0.15 g of sodium hydroxide (pellets) to 22.8 g of anhydrous methanol. Heat to 70°C to dissolve the alkali. This reagent may be stored for future use

Place 0.8 ml of the methanol alkali reagent in a test tube and heat to 70°C. Add 2.0 g of the sample of triglyceride preheated to 80°C. Stir and heat at 80°C until glycerol separates. Allow to stand at 80°C for 5 minutes and then decant the methyl esters. Evaporate any remaining methanol from the esters under reduced pressure after decanting

**Fatty Acids**—Place 1 liter of reagent grade methanol in a 2 liter flask. Weigh the flask and contents and then cool them in an ice bath. With the flask still in the bath boron trifluoride is bubbled through a glass tube into the methanol until 125 g are taken up. This operation should be performed in a good fume hood and the gas should not be allowed to flow so fast that white fumes emerge from the flask. The boron trifluoride must be flowing through the tube before it is placed in and until it is removed from the methanol or the liquid may be drawn into the gas cylinder valve system

**Esterification Procedure.**—Place 100–200 mg. of fatty acids in a 20 x 150 mm. test tube, and add three ml. of boron trifluoride-methanol reagent. Place the mixture on a steam bath and allow to boil for 2 minutes. Recover the esters by the appropriate procedure following.

**For Acids of More Than 10 Carbons.**—Wash the boiled mixture into a 125-ml. separatory funnel with 30 ml. of petroleum ether (b.p. 40–60°C., reagent grade, redistilled) and add 20 ml. of distilled water. Shake the funnel vigorously and allow the layers to separate. Drain and discard the aqueous-methanol layer. Remove the petroleum ether layer and filter through filter paper into a 50-ml. beaker. Evaporate on a steam bath and then remove any remaining solvent under reduced pressure.

**For Acids of Less Than 10 Carbons.**—Transfer the boiled mixture into the separatory funnel with 20 ml. of water, mix the contents and allow the layers to separate. Remove the top ester layer from the lower aqueous layer, and filter or centrifuge to remove small amounts of entrapped water.

**Procedure.**—With gas flowing through the apparatus, adjust to the desired operating temperature and record a baseline to check the stability of the instrument. Whatever the selected temperature, it must be kept constant at this level. A range of 180°–210°C. will probably include the temperature levels used by most of the laboratories in the country. A new column should be conditioned before use by holding at the operating temperature with gas flowing through it for 24 hours.

The properly selected gas flow rate will permit elution of the C-18 and shorter chain acids in 30 minutes. The inlet pressure and gas flow rate necessary to accomplish this will vary between columns and instruments used but will be relatively constant for a single apparatus. The inlet gas pressure should not exceed 40 pounds per square inch.

Use a suitable hypodermic syringe (0.01-ml. capacity) to introduce 2 to 5 microliters (0.002–0.005 ml.) of the esters into the sample inlet port. A small peak should show on the recorder chart due to air. This serves as a reference point marking the introduction of the sample.

Watch the recorder pen to see that peaks do not go off scale. If automatic attenuation is not provided change the setting of the attenuator as necessary to keep the peaks on the chart paper. Mark the setting on the chart. After all the peaks have been traced and the pen has returned to the baseline remove the chart for calculation.

**Calculation.**—Determine the area of each peak. This is conveniently accomplished by drawing lines intersecting the baseline and tangent to the sides of the peak. Determine the area of the resulting triangle by multiplying the height (corrected for any change in attenuation) by half the base. Obtain the sum of the areas under all of the peaks and calculate the percentage represented by each. Greater accuracy may be obtained by deriving calibration factors from the analysis of samples of known composition. However, the former method of calculation will suffice for most cases.

Identify the peaks by their relative position on the chart, that is the distance from the air peak to the various sample component peaks. Compare these with results obtained from the analysis of known mixtures run on the same column under the same conditions.

# NATURAL FATS

## ISOLATED TRANS ISOMERS

### INFRARED SPECTROPHOTOMETRIC METHOD<sup>3</sup>

For the accurate determination of *trans* isomers it is necessary to prepare or otherwise obtain pure samples of methyl elaidate or trielaidin (99%) and to determine the absorptivity of these with the same spectrophotometer and according to the same conditions under which the analysis will be performed. The elaidate serves as the primary reference standard for the analysis of long chain fatty acids which are analyzed as methyl esters if present in amounts of less than 15%. Trielaidin is the primary reference standard for the analysis of glycerides. Because primary standards of high purity are not readily available it is convenient and satisfactory to establish and use secondary standards of esters and glycerides for reference purposes. These should be checked against the primary standards to assay the known *trans* isomer content.

**Procedure** Weigh 2.000 ( $\pm 0.0002$ ) g of sample and place in a 10 ml volumetric flask. Add carbon disulfide to dissolve the sample and then make to volume with the same solvent. The concentration should be such that the transmittance will be within 20 and 70% at the *trans* absorption maximum in the absorption cell selected.

Use fixed thickness (0.2 to 2.0 mm) absorption cells with NaCl or KBr windows. Determine the absorption of the sample with a suitable infrared spectrophotometer over the region 9–11  $\mu$  with carbon disulfide in the matched cell. Follow manufacturer's directions for operation of the spectrophotometer. A maximum at about 10.36  $\mu$  is exhibited in the spectrum if isolated *trans* groups are present.

Make the calculations utilizing the baseline technique. Draw a line on the chart of the absorption curve through the point of maximum absorption to the baseline joining the points 10.02  $\mu$  and 10.64  $\mu$  for methyl esters, 10.10  $\mu$  and 10.63  $\mu$  for fatty acids and to the baseline joining the points 10.03  $\mu$  and 10.67  $\mu$  for triglycerides.

Measure the distance from the zero line of the recorder chart to the absorption peak. Calculate the fractional transmission as the distance to the absorption peak divided by the distance to the baseline. Convert to absorbance and calculate the absorptivity ( $a$ )

$$a = \frac{A}{bc}$$

where  $A$  is the absorbance ( $\log_{10} \frac{I_0}{I}$ )  $I$  is transmittance  $b$  is the cell thickness in cm and  $c$  is the concentration in grams per liter of the sample dilution tested.

Calculate the % *trans* isomer as methyl elaidate, elaidic acid or trielaidin from the equation

$$\% \text{ trans component} = \frac{100a_s}{a_k}$$

where  $a_s$  and  $a_k$  are the absorptivities of the sample and standard respectively.

<sup>3</sup> O'Connor, R. T. J. Am. Oil Chemists Soc. 36, 627 (1959).



## SOLID FATTY ACIDS

MODIFIED TWITCHELL METHOD<sup>29</sup>

This method provides a means for the separation and determination of solid fatty acids. The lead salts of the saturated acids are somewhat soluble under the conditions of the test and no correction is made for unsaponifiable matter. This method is applicable to animal and vegetable fats and oils except those of the coconut oil group, butterfat or other fats, and oils containing low molecular weight saturated fatty acids. The method is not satisfactory for oils containing high molecular weight unsaturated fatty acids such as are obtained from rape and mustard seed. The method is not applicable if rosin acids are present.

*Procedure.*—Heat about 25 g. of the melted fat on a steam or water bath with about 15 g. of potassium hydroxide which has been dissolved in a few ml. of distilled water. Add 25 ml. of alcohol. Continue heating with occasional stirring until the soap begins to dry out on the sides of the beaker. From then on stir continuously until the soap becomes a pasty jelly-like mass but avoid baking on the sides or bottom of the sample during this entire period. Oxidation or burning must be avoided. Add 200 ml. of distilled water and heat to dissolve all of the soap. Add, while stirring, sufficient hydrochloric acid (sp. gr. 1.19) to make the solution acid as indicated by methyl orange. Heat until the contents of the beaker can be poured freely and then transfer into a 500-ml. separatory funnel, washing the beaker with 100 to 150 ml. of ethyl ether and transferring this to the funnel also.

Stopper the funnel and invert carefully several times so that all of the fatty acids will be dissolved in the ether. Allow the aqueous and ether layers to separate and drain off the lower (aqueous) layer. Add about 50 ml. of water to the funnel and again invert a few times. Allow to separate and drain. Continue in this fashion until the washings show no trace of acid as indicated by methyl orange indicator. Three washings are usually sufficient. When the last washing is made, the separation must be as complete as possible, avoiding leaving any water in the ether portion containing the mixed fatty acids.

Withdraw the ether solution into an Erlenmeyer flask, add anhydrous sodium sulfate, stopper, allow to stand for 1 hour with frequent stirring, and then filter through a dry filter paper into a beaker or Soxhlet flask. Evaporate all of the ether on a water bath under a gentle stream of nitrogen gas. Preserve the fatty acids in a glass-stoppered flask, store under nitrogen, and maintain in a refrigerator at 4° to 10°C.

Weigh accurately a quantity of sample that will yield from 0.9 to 1.5 g. of solid fatty acids into a 250-ml. beaker. The sample weight must never exceed 5 g. even if the yield of solid acids is less than 0.9 g. Place 1.5 g. of powdered lead acetate into another 250-ml. beaker. Add 50 ml. of alcohol to each beaker, cover each with a watch glass and bring both to boil on a water bath or low temperature hot plate. Transfer the alcoholic lead acetate to the alcoholic fatty acids, stirring continuously while so doing and bring to the boiling temperature. Cool to room temperature (20° to 25°C.) and place in an ice and water bath at 15°C. for 2 hours or in a refrigerator at about 15°C. overnight (16 hours).

Filter through a Büchner funnel containing a snugly fitting filter paper using suction to aid filtration. Wash the beaker and filter paper with four 50-ml. portions of alcohol which have been previously cooled to 15°C. After the alcohol has

<sup>29</sup> Twitchell, E., Ind. Eng. Chem., 13, 806, 1921.

filtered from the lead soap, transfer the contents of the filter paper quantitatively back to the beaker originally containing the fatty acids. Use about 100-ml of warm alcohol (50°C) to wash off all of the soap making certain that no particles of soap remain in the funnel. Test the filtrate for an excess of lead acetate by adding a few drops of sulfuric acid to 40 to 50 ml of the filtrate. If the test solution becomes turbid, it is satisfactory. If no cloudiness appears, the original sample was too large and the determination must be repeated from the beginning with a smaller sample. The filtrate is discarded.

Add 0.5 ml of glacial acetic acid to the alcoholic soap solution and heat until all soap is dissolved. Cool to room temperature (20° to 25°C). Continue cooling at 15°C in a refrigerator or overnight and then filter and wash as previously directed. Transfer again to the original beaker using 75 ml of ethyl ether instead of warm alcohol to remove the lead soap. Add 20 ml of nitric acid to the beaker to separate the fatty acids and then transfer the contents to a 500 ml separator funnel. Add 5 ml of nitric acid to the beaker to facilitate the final transfer. Finally wash the beaker thoroughly into the funnel with 100 ml of ethyl ether. Add 50 to 100 ml of distilled ether to the funnel and invert a few times to wash the ether solution. Allow the layers to separate and drain the aqueous layer. Repeat this until the washings are no longer acid to methyl orange.

Withdraw the ether solution into previously dried and tared 250 ml beaker or Soxhlet flask. Wash the funnel with a few ml of ethyl ether and add this to the beaker. Evaporate the ether on a water bath under a gentle stream of clean and dry nitrogen gas. Dry for 1 hour in an air oven at  $101^{\circ} \pm 1^{\circ}\text{C}$ . Cool to room temperature in a desiccator and weigh. Repeat to constant weight. Constant weight is attained when the loss in weight does not exceed 0.1% in successive 1 hour drying periods.

$$\% \text{ Solid fatty acids} = \frac{\text{Weight of solid acids} \times 100}{\text{Wt. of sample}}$$

### EPOXY GROUPS<sup>1</sup>

The epoxy or oxirane compounds contain a three membered ring with two adjacent carbon groups. These compounds are not usually found in natural fats but they are produced during the autoxidation of unsaturated oils and fatty acids.

**Apparatus.** A buret and bottle assembly protected with drying tubes to maintain the standard solution free of contamination with moisture either from the atmosphere or otherwise. It is important that the titration be performed in a closed system to avoid the loss of hydrogen bromide. Provide a closed system by attaching the titration flask to the buret tip with a 1 hole rubber stopper. The hole in the stopper should be spherical so as to take the buret tip snugly with a small side opening to permit the air to escape from the flask during titration.

A magnetic stirrer of any suitable type with round magnetic stirring bars covered with "Teflon" or equivalent protective covering.

**Reagent.**—Prepare 0.1 N hydrogen bromide in glacial acetic acid by bubbling HBr gas through glacial acetic acid to approximately 0.1 N. Weigh 0.4 g of potassium acid phthalate, predried for 2 hours at 120°C. Dissolve the phthalate in 5 ml of glacial acetic acid and titrate the acid bromide solution using 5 drops of crystal violet indicator. Standardize the hydrogen bromide solution daily.

$$\text{Normality of the HBr solution} = \frac{\text{Wt. of phthalate}}{0.2042 \times (\text{titration-ml})}$$

**Procedure.**—Weigh  $0.3$  to  $0.5 \pm 0.0001$  g. of the sample into a 50-ml. Erlenmeyer flask. Dissolve the sample in 5 ml. of benzene (in case of epoxy resins, use chlorobenzene). Add 5 drops of the crystal violet indicator (0.1 g. in 100 ml. of glacial acetic acid) and a stirring bar.

Place the rubber stopper in position and lower the tip of the buret until it discharges just above the solution. This is important to avoid the loss of hydrogen bromide.

Stir and titrate the sample (rapidly at first) with the 0.1 *N* glacial acetic acid-hydrogen bromide solution to a bluish-green end point. Control the rate of the magnetic stirrer so as to avoid splashing.

$$\% \text{ Oxirane oxygen} = \frac{\text{Titration} \times N \times 1.6}{\text{Wt. of sample}}$$

### THE DETERMINATION OF FAT CONTENT <sup>1, 4</sup>

Conventional methods for the determination of the oil or fat content of various animal and vegetable source materials are based on (a) a preliminary treatment of the sample to render the fat extractable followed by (b) extraction with a fat solvent such as ethyl or petroleum ether (c) and finally a gravimetric estimate of

TABLE 33-15. SUMMARY OF EXTRACTION METHODS FOR DETERMINING THE OIL CONTENT OF SOME SOURCE MATERIALS

<i>Product</i>	<i>Sample (grams)</i>	<i>Solvent</i>	<i>Preparation of Sample</i>	<i>First Extraction (hrs.)</i>	<i>Regrind</i>	<i>Second Extraction (hrs.)</i>
Cottonseed	4-5	Petr. ether	Delinted, predried and finely ground	4	None	None
Soybeans	2	Petr. ether	Predried and finely ground	2	Reground in mortar, 100 strokes	3
Peanuts	2	Petr. ether	Predried and sliced	2	Reground in mortar, 100 strokes	2
Whole tung fruit	5	Petr. ether	Ground	4	None	None
Sesame seed	2	Petr. ether	Ground	2	Reground	3
Oilseed cake and meal	5	Petr. ether	Ground	3	None	None
Soy flour high fat	2	Petr. ether	Mixed	5	None	None
Meat	3-4	Petr. ether	Predried	4	None	None

the residue after removal of the solvent. The preliminary treatment usually involves the removal of most of the moisture followed by grinding to reduce the particle size. The extraction is performed with a Butt or Soxhlet type apparatus. Certain products require regrinding in a mortar after some of the oil is removed in order to obtain a sufficiently fine grind.

There is no single method applicable to all oil bearing materials. Because of differences in the composition and physical character of these, each method must be tailored to the specific product. For more details the reader is referred to more detailed procedures. Table 33-15 outlines briefly the methods used with the most common fat source materials.

The methods that have been presented here constitute those most commonly used for the analysis of fats and oils for purposes of production control and trading. References to less frequently used methods are presented below.<sup>30</sup>

<sup>30</sup> Determination of antioxidants: Anglin C. Mahon J. H. and Chapman R. A. *J. Agr. and Food Chem.* 4, 1018, 1956; bleach tests: see reference <sup>30</sup>; diglycerides: Quinlin P. and Weiser H. J. Jr. *J. Am. Oil Chemists Soc.* 35, 327, 1958; gossypol (total): Pons W. A. Jr., Pittman R. A. and Hoffpauer C. L. *J. Am. Oil Chemists Soc.* 35, 93, 1958; gossypol (free): Schramm G. and Benedict J. H. *J. Am. Oil Chemists Soc.* 35, 371, 1958; hydrocarbon oils: Williams K. A. *J. Assoc. Off. Agr. Chemists* 26, 506, 1943; methyl esters: Allen R. R. and Buswell R. J. *J. Am. Oil Chemists Soc.* 30, 123, 1953; and reference <sup>3</sup>; oxidized fatty acids: International Union of Pure and Applied Chemistry, Standard Methods for the Analysis of Oils and Fats, Paris, 1954; solubility tests: see reference <sup>1</sup>; x-ray spectroscopy: Lutton E. S. *J. Am. Oil Chemists Soc.* 27, 276, 1950.

## Chapter 34

# FERTILIZERS

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The purpose of this chapter is to aid the analytical chemist whose work includes occasional analyses of fertilizers by giving him the convenience of a select compilation of reliable methods. The chemist confronted with more extensive analytical work on fertilizers should refer to the more comprehensive treatments that are cited, particularly the *Official Methods of Analysis* of the Association of Official Agricultural Chemists (AOAC).

### SAMPLING AND SAMPLE PREPARATION<sup>1,2</sup>

Most fertilizers are mixtures of unlike materials with a marked tendency toward segregation. Sampling problems associated with segregation are intensified when the material is placed in bags or in piles so that, when possible, samples should be taken in increments from a conveyor belt or from a stream of the material before it is loaded into the final container. The increments must be large enough to be representative of a cross-section of the stream, and enough increments must be taken to be representative of the period of production. Under no circumstances should the sample be dipped from the top of the material on a conveyor belt or from the side of a stream.

The device generally used for sampling fertilizer in piles or in bags is a slotted tube with a pointed end. A very narrow sampler should be avoided as insertion of the sampler induces segregation, and a narrow sampler with a narrow slot is likely to admit coarse and fine materials in disproportionate amounts.

*Reduction of Gross Sample.*—The size of the gross sample will vary with the quantity of material sampled; it may weigh several pounds. When it consists of particles 20 mesh or finer, it may be reduced to approximately 8 oz. by means of a riffle. Samples containing coarser particles should first be ground to minus 20 mesh.

The final sample of a mixed fertilizer should be crushed to pass a 35-mesh screen. Even finer grinding is desirable when the gross sample contains materials that vary widely in particle size. The process of grinding frequently segregates unlike materials, and the sample must be reconstituted after grinding.

<sup>1</sup> Association of Official Agricultural Chemists, *Official Methods of Analysis*, 9th Ed., Secs. 2.001, 2.007, 1960.

<sup>2</sup> Tomlinson, R. C., *Comprehensive Analytical Chemistry*, Vol. 1A, edited by Cecil L. Wilson and David W. Wilson, Elsevier Publishing Company, New York, pp. 36-75, 1959.

Fertilizer materials, if homogeneous, need not be crushed finer than 20 mesh. Some, such as superphosphate, cannot be ground any finer.

### WATER<sup>3</sup>

Water in fertilizers is determined as "total water" or as "free water." Total water is determined by thermally drying materials which lose only water when heated. Many fertilizer materials (superphosphate and diammonium phosphate for example) should not be dried by heating; instead, they are vacuum dried in a desiccator over a strong neutral desiccant, such as anhydrous magnesium perchlorate, and the loss in weight is reported as free water. Only free water should be determined on mixed fertilizers whose formulations are not known.

### TOTAL WATER

*Procedure.*—Put about 2 g of sample into a tared flat form glass weighing bottle, with cover, and record the total weight. Heat in a well ventilated oven at 105°C. for 1 hour with cover off. Remove from the oven, cover, cool in a desiccator, and weigh.

When it is known that drying at a higher temperature will not decompose the sample a higher temperature is used. Thus, potassium salts customarily are dried at 130°C.

### FREE WATER

*Procedure.*—Place in a tared flat form glass weighing bottle approximately 2 g of sample and determine the gross weight of bottle, cover and sample. Place uncovered in a desiccator containing anhydrous magnesium perchlorate (Dehydrite) at 25° to 30°C. Evacuate the desiccator to at least 20 in. of vacuum. After 16 to 18 hours remove and weigh.

### KARL FISCHER METHOD<sup>4,5</sup>

The Karl Fischer titration method (pp 275 and 526) has been used successfully for the routine determination of water in such fertilizer materials as ammonium nitrate and diammonium phosphate. It can be used also for the determination of total water in some, but not all, hydrates. Rational application of the method to mixtures requires a knowledge of the compounds present.

### NITROGEN

Nitrogen in fertilizers may be present as a variety of inorganic and organic compounds. Some of the nitrogen may be derived from organic residues such as fish scrap and castor pomace. Total nitrogen is always determined, but specific forms of nitrogen need be determined only when the fertilizer has to be characterized for special purposes.

The basis for most methods for the determination of total nitrogen is the liberation of ammonia with an alkali and absorption of the ammonia in standard acid.

<sup>3</sup> Association of Official Agricultural Chemists. Official Methods of Analysis, 9th Ed. Secs. 2012, 2015, 1950.

<sup>4</sup> Engelbrecht, R. M., Drexler, S., and McCoy, F. A., J. Agr. Food Chem., 4, 786, 1956.

<sup>5</sup> Mitchell, J., Jr., and Smith, D. M., Aquametry, Interscience Publishers, Inc., New York 1948.

Nitrogen originally present in other forms therefore must be converted to the ammoniacal form. Nitrates can be reduced to ammonia by nascent hydrogen in alkaline or acid media. Nitrogen in other forms offers varying degrees of resistance to conversion; it generally can be changed to ammoniacal nitrogen by a Kjeldahl digestion—an empirical procedure in which the sample is fumed with sulfuric acid. Various modifications of the procedure are designed to hasten the digestion by means of catalysts, to prevent loss of nitrogen and to ensure complete conversion of refractory nitrogen compounds.

### TOTAL NITROGEN—KJELDAHL METHOD FOR NITRATE-FREE SAMPLES<sup>6,7,8,9</sup>

The Kjeldahl method is suited for fertilizers whose nitrogen content is entirely in organic and ammoniacal forms. Nitrates are lost in this procedure, either through displacement by sulfuric acid or through reaction with chlorides to form nitrosyl chloride.

**Reagents.** Sulfuric Acid.— $H_2SO_4$ , 95 to 98%, nitrogen free.

Mercuric Oxide or Mercury.

Potassium Sulfate.—Nitrogen free.

Sulfide or Thiosulfate Solution.—Dissolve 40 g. of potassium sulfide or sodium sulfide in water and dilute to 1 liter. If thiosulfate is preferred, dissolve 80 g. of sodium thiosulfate pentahydrate in water and dilute to 1 liter.

Sodium Hydroxide Solution.—Dissolve 450 g. of sodium hydroxide in 1 liter of water.

Zinc Granules.

Sulfuric Acid.—0.5 *N*.

Sodium Hydroxide.—0.5 *N*.

Methyl Red—Methylene Blue Indicator.—Dissolve 1.250 g. of methyl red and 0.825 g. of methylene blue in 1 liter of 95% ethanol. Store in a dark bottle.

**Procedure.**—Transfer a sample containing 200 to 300 mg. of nitrogen to an 800-ml. Kjeldahl flask. Add 0.7 g. of mercuric oxide or 0.65 g. of metallic mercury, 15 g. of potassium sulfate, and 25 ml. of sulfuric acid. If a sample larger than 2 g. is required, add an additional 10 ml. of  $H_2SO_4$  per gram of sample over 2 g.

Place the flask in an inclined position on a heater that can be regulated to bring 250 ml. of water at 25°C. to a rolling boil in 5 minutes ("recommended rate"). Heat gently until frothing ceases. If frothing is excessive, add a small piece of paraffin. Increase the heat to the "recommended rate," boil until the solution clears, and continue the digestion for at least 30 minutes more. When organic materials are present, increase the time of digestion to 2 hours. If necessary, add more sulfuric acid to replace that lost by prolonged fuming. Cool, add 250 ml. of water, and again cool below 25°C.

Add a few pieces of granular zinc or a few glass beads to prevent bumping. Precipitate the mercury by adding 25 ml. of sulfide or thiosulfate solution while shaking the flask vigorously. Add 50 ml. of the concentrated solution of sodium hydroxide by pouring it gently down the side of the flask to minimize mixing

<sup>6</sup> Association of Official Agricultural Chemists, Official Methods of Analysis, 9th Ed., Secs. 2.034, 2.035, 2.036, 1960.

<sup>7</sup> Bates, R. W., Etheredge, M. P., and Quackenbush, F. W., J. Assoc. Offic. Agr. Chemists, 38, 56–61, 1955.

<sup>8</sup> Davis, H. A., and Miles, S. R., Ibid., 39, 550–58, 1956.

<sup>9</sup> Johnson, A. H., and Green, J. R., Ind. Eng. Chem., Anal. Ed., 2, 2–4, 1930.

with the acid solution (The sodium hydroxide and sulfide solutions can be mixed first then added if desired) Immediately connect the flask to a distilling bulb (a Davison scrubber is recommended) on a condenser whose tip just dips into 50 ml of 0.5 N sulfuric acid in a 500 ml Erlenmeyer flask.

Rotate the Kjeldahl flask to mix the contents then boil the solution. Distill at a rate that yields 200 ml of distillate in about 45 minutes. Lower the receiver to bring the condenser up above the liquid and continue the distillation for about 1 minute. Wash the condenser tip.

Add 5 drops of methyl red-methylene blue indicator to the distillate and titrate the excess acid with 0.5 N alkali to a faint green end point. Correct for a blank determination made with the reagents.

Calculation —

$$\text{N per cent} = \frac{\text{net milliliters of H}_2\text{SO}_4 \times \text{normality} \times 1.4008}{\text{weight of sample, grams}}$$

### TOTAL NITROGEN—REDUCED IRON METHOD<sup>10 11 12 13 14</sup>

The reduced iron method is used for the determination of total nitrogen in nitrate-chloride mixtures and in liquid fertilizers—materials that are unsuited to conventional Kjeldahl procedures. Reduced iron is added to a water solution of the sample; sulfuric acid is added and nitrates are reduced to ammonium salts by nascent hydrogen. The solution is boiled, evaporated to fumes in the presence of a catalyst, then Kjeldahlized to convert the more refractory compounds of nitrogen to ammonium salts.

**Reagents** Iron Metal—Powder reduced by hydrogen

Sulfuric Acid—(1 + 1)

Sulfuric Acid—0.5 N

Sodium Hydroxide—0.5 N

**Procedure**—For dry mixed fertilizers transfer a sample containing 125 to 150 mg total nitrogen (but in no event more than 42 mg of nitrate nitrogen) to a 800 ml Kjeldahl flask. Add 5 g of reduced iron powder and 50 ml of water. Allow to stand for 15 minutes with occasional shaking to dissolve soluble salts.

For a soluble nitrate salt or a liquid fertilizer so dilute a sample that a 50 ml aliquot contains the specified amount of nitrogen. Transfer the aliquot to a 800 ml Erlenmeyer flask and add 5 g of reduced iron.

Add 45 ml of (1 + 1) sulfuric acid and set aside until visible reaction ceases. When the sample contains refractory nitrogen compounds that require prolonged digestion increase the amount of (1 + 1) sulfuric acid to 80 ml. If urea is present dilute to 200 ml before the solution is heated (thus ensuring hydrolysis of the urea prior to the Kjeldahl digestion).

Heat the solution to boiling and evaporate to 50 ml. Add 0.7 g of mercuric oxide and continue the digestion rotating the flask frequently as fumes appear. Continue the digestion for 1 hour or until the contents thicken and cling to the

<sup>10</sup> Association of Official Agricultural Chemists Official Methods of Analysis 9th Ed Secs 2.038-2.039 1960

<sup>11</sup> Berliner J. F. T. Ind Eng Chem 28, 517-22 1936

<sup>12</sup> Ford O. W. J Assoc Offic Agr Chemists 39, 763-65 1956

<sup>13</sup> J Assoc Offic Agr Chemists 41, 32 1958

<sup>14</sup> Ulsch K. Z anal Chem 30, 175 1831



sides of the flask. Do not evaporate to dryness. Cool, add 200 ml. of water, and cool below 25°C.

Add a few pieces of zinc or several glass beads to prevent bumping, and continue with the Kjeldahl procedure as outlined above.

### AMMONIACAL AND NITRATE NITROGEN<sup>15</sup>

When a fertilizer contains nitrogen only in ammoniacal and nitrate forms, the nitrate can be reduced in alkaline medium and the ammonia distilled into standard acid. This technique, the Devarda method, requires less time than the Kjeldahl method.

*Reagents.* Devarda Alloy.

Sodium Hydroxide.—42% by weight.

Methyl Red—Methylene Blue Indicator.

Sulfuric Acid.—0.5 *N*.

Sodium Hydroxide.—0.5 *N*.

*Procedure.*—Transfer a sample containing 200 to 300 mg. of nitrogen to an 800-ml. Kjeldahl flask. Add 350 ml. of water to dissolve the soluble salts. (When the nitrogen in the fertilizer is known to be soluble in water, the accuracy may be improved by dissolving a larger quantity and analyzing a suitable aliquot.) Add 3 g. of Devarda alloy, then gently run 5 ml. of 42% sodium hydroxide solution down the side of the flask (minimize mixing). Immediately connect the flask, by means of a Davison scrubber, to the condenser, the tip of which just dips into 50 ml. of 0.5 *N* sulfuric acid in a 500-ml. Erlenmeyer flask.

Rotate the flask to mix the contents, then gradually heat the solution to boiling. Distil at a rate that yields 250 ml. of distillate in 1 hour. Titrate the excess acid in the receiver as described above for the determination of total nitrogen.

### AMMONIACAL NITROGEN<sup>16,17</sup>

The determination of ammoniacal nitrogen is straightforward when all the nitrogen is in ammoniacal and nitrate forms. Digestion with sodium hydroxide evolves ammonia, which is absorbed in an excess of standard acid. Magnesium oxide is not recommended for the distillation; it will not displace ammonia from some water-insoluble ammonium compounds.

Urea, when present, partly decomposes, and the liberated ammonia leads to inaccurately high results. Satisfactory results can be obtained by adding the sodium hydroxide as an alcoholic solution and conducting the distillation under reduced pressure at 40°C.

### NITRATE NITROGEN—INDIRECT METHOD<sup>18</sup>

Nitrate nitrogen, when alone, can be determined by the reduced iron method or by the Devarda method; when ammoniacal nitrogen is also present, the two forms of nitrogen are determined together, ammoniacal nitrogen is determined on a separate sample, and nitrate nitrogen is determined by difference.

The residue from an ammoniacal nitrogen determination should never be used

<sup>15</sup> Association of Official Agricultural Chemists, *Official Methods of Analysis*, 9th Ed., Sec. 2.043, 1960.

<sup>16</sup> Yee, J. Y., and Davis, R. O. E., *Ind. Eng. Chem., Anal. Ed.*, 7, 259–61, 1935.

<sup>17</sup> Yee, J. Y., and Davis, R. O. E., *J. Assoc. Offic. Agr. Chemists*, 20, 104–7, 1937.

<sup>18</sup> Brabson, J. A., and Karchmer, J. H., *J. Assoc. Offic. Agr. Chemists*, 28, 142–47, 1945.

for the determination of nitrate by the Devarda method. Silica dissolved from the glassware by the sodium hydroxide interferes with the reduction of nitrate.

### NITRATE NITROGEN—DIRECT METHOD<sup>19, 20</sup>

The nitrate nitrogen content of complex fertilizers can be determined directly by an oxidimetric method provided the fertilizers contain no other oxidizing agents.

A solution of the sample is treated with an excess of a standard ferrous sulfate solution containing sodium chloride. Sulfuric acid is added and the solution is boiled to reduce the nitrate to nitric oxide. Excess ferrous sulfate in the final solution (cooled and diluted) is titrated with a standard solution of potassium permanganate. A correction factor is necessary when the sample contains urea.

### UREA NITROGEN—TITRIMETRIC<sup>21, 22, 23, 24</sup>

An enzymatic hydrolysis of urea to ammonia and carbon dioxide forms the basis of a titrimetric method for the determination of urea in mixed fertilizers containing phosphate. Phosphate and calcium are first removed by treatment with barium hydroxide and sodium carbonate. An aliquot is then acidified and sparged with nitrogen to remove carbon dioxide. The resultant solution is neutralized with sodium hydroxide and the enzyme urease is added to hydrolyze the urea. An excess of standard acid is added to neutralize the ammonia and to evolve the carbon dioxide. Finally the excess acid is titrated with standard sodium hydroxide.

**Reagents** Urease Powder—Jack bean

**Neutral Urease Solution 1%**—Add 1 g of urease powder to 100 ml of water and shake for 5 minutes. Dilute 10 ml of the suspension with 50 ml of water and add 4 drops of methyl red-methylene blue indicator and neutralize to the purple color with 0.1 N hydrochloric acid. Back titrate with 0.1 N sodium hydroxide to the green end point. Deduct the amount of standard base from the standard acid to determine the amount of standard acid required to neutralize 10 ml of the urease solution. Add the calculated amount of acid to neutralize the remaining 90 ml of solution and mix thoroughly.

**Hydrochloric Acid—2 N**

**Barium Hydroxide—Saturated**

**Sodium Carbonate**—Dissolve 10 g of the anhydrous salt in 100 ml of water in Octinol or Silicone type Antifoaming Agent

**Nitrogen**

**Sodium Hydroxide—0.1 N**

**Hydrochloric Acid—0.1 N**

**Methyl Red-Methylene Blue Indicator**—Or Methyl Purple a proprietary product of Fleisher Chemical Company

**Procedure**—Place a sample containing not more than 1 g of urea on a 15 cm Whatman No. 12 or equivalent fluted filter paper in a funnel. Samples with a gross weight greater than 10 g cannot be handled readily. Wash 20 times with 15

<sup>19</sup> Engelbrecht R. M. and McCoy F. A. *Anal. Chem.* 28, 1619-21, 1956

<sup>20</sup> Leithe W. *Ibid.* 20, 1082-84, 1948

<sup>21</sup> Association of Official Agricultural Chemists. *Official Methods of Analysis* 9th Ed. Secs. 2.0.1, 2.0.5, 1960

<sup>22</sup> Davis H. A. *J. Assoc. Offic. Agr. Chemists* 42, 494-99, 1959

<sup>23</sup> Morgan W. A. and Harford E. I. *Ibid.* 41, 637-39, 1958

<sup>24</sup> Yee J. Y. and Davis R. O. E. *Ind. Eng. Chem. Anal. Ed.* 7, 259-61, 1935

ml. increments of water, and catch the washings in a 500-ml. volumetric flask (use a 1-liter flask when working with samples high in phosphate). Add 75 to 100 ml. of saturated barium hydroxide solution to precipitate phosphate. Test for complete precipitation by adding a few drops of the barium solution to the supernatant liquid, and add more as required. Add 20 ml. of sodium carbonate solution to precipitate excess barium and soluble calcium salts. Let settle and test for complete precipitation by adding more sodium carbonate.

Dilute to volume, mix thoroughly, and filter on a 15-cm. Whatman No. 12, or equivalent fluted paper. Transfer a 50-ml. aliquot to a 200-ml. Erlenmeyer flask and add 2 drops of mixed indicator. Acidify with 2 *N* hydrochloric acid to a purple color and add a 3-drop excess. Bubble nitrogen through the solution for 5 to 10 minutes to remove carbon dioxide. Neutralize the solution to the green end point with 0.1 *N* sodium hydroxide. Add 20 ml. of neutral urease solution per 0.1 g. of urea, stopper the flask, and let stand at 40°C. for 20 minutes. Cool the solution by immersing the flask in ice water. Titrate immediately with 0.1 *N* hydrochloric acid to a purple end point, then add about 5 ml. in excess. Record the amount of acid.

Add sufficient octanol or other antifoaming agent to prevent frothing and again purge the solution with nitrogen. Back-titrate to the green end point with 0.1 *N* sodium hydroxide. The net volume of standard acid is a measure of the urea in the sample.

Calculation.—

$$\text{Urea, per cent} = \frac{\text{milliliters } 0.1 \text{ } N \text{ HCl} - \text{milliliters } 0.1 \text{ } N \text{ NaOH} \times 0.3003}{\text{weight of sample in aliquot}}$$

#### UREA—SPECTROPHOTOMETRIC <sup>25</sup>

Urea (in solution) can be determined quite rapidly through its reaction with *p*-dimethylaminobenzaldehyde; the color intensity of the complex thus formed is measured with a spectrophotometer. (As the reagent itself is highly colored, a good spectrophotometer is necessary.) Close control of temperature is required, as the reaction is temperature-sensitive. Fertilizers contain few known interferences except ammonia, which interferes only when its mole ratio to urea exceeds 10.

#### BIURET—SPECTROPHOTOMETRIC <sup>26</sup>

Biuret, a product of the thermal decomposition of urea, has herbicidal properties. It is determined in urea and occasionally in fertilizers that have been heated sufficiently to decompose urea.

Biuret reacts with copper salts in an alkaline medium to give an intense violet color ("biuret reaction"). Because a hydrous copper oxide precipitate interferes with measurement of the color intensity, it is generally removed by filtration, but in the method referred to here, sodium potassium tartrate forms a soluble complex with excess copper and eliminates the filtration step.

The method is suited for the determination of biuret in urea pyrolyzates containing triuret and cyanuric acid. Ammonia can cause high results but is easily removed with a cation exchange resin. The method appears promising for the determination of biuret in mixed fertilizers, provided ammonia and alkaline earths are removed by a treatment with a resin.

<sup>25</sup> Watt, G. W., and Chrisp, J. D., *Anal. Chem.*, **26**, 452-53, 1954.

<sup>26</sup> Ellis, G. C., and Formaini, R. L., *J. Agr. Food Chem.*, **3**, 615-18, 1955.

## PHOSPHORUS\* \*\*

Phosphorus in fertilizers is largely in the form of inorganic compounds although some organic compounds are found in specialty fertilizers. Phosphorus is always most often in the form of orthophosphate but current trends in fertilizer technology indicate that increasing amounts of other phosphates should be expected. All methods for determining phosphorus in fertilizers are based on reactions of orthophosphoric acid so techniques for decomposing fertilizers for analysis must convert all forms of phosphorus to the orthophosphate.

Phosphate fertilizers in the United States are sold on a basis of chemically available phosphorus rather than total phosphorus although these quantities may be the same for some materials. Chemically available phosphorus is the difference between total phosphorus and citrate-insoluble phosphorus—the portion which remains after the sample has been subjected to successive extractions with water and neutral ammonium citrate.

## DECOMPOSITION OF SAMPLE

Various procedures may be used for decomposing fertilizers and converting the phosphorus to orthophosphate. The three techniques described here are adequate for most compounds and mixtures.

## INORGANIC ORTHOPHOSPHATES THAT MAY CONTAIN SOME ORGANIC MATTER

**Procedure (Nitric Hydrochloric Acid Digestion)**—To a sample (0.5 to 20 g) in a 250 ml Erlenmeyer flask or beaker add 30 ml of nitric acid and 5 ml of hydrochloric acid. Boil gently for about 15 minutes then cool. Dilute to volume in a volumetric flask and filter through a dry filter.

## SAMPLES CONTAINING NON-ORTHOPHOSPHATIC IRON AND ALL MINERAL PHOSPHATES OR BASIC SLUG

**Procedure (Hydrochloric Nitric Acid Digestion)**—Follow the procedure in the preceding paragraph but add 40 ml of hydrochloric acid and 3 to 10 ml of nitric acid. Hydrochloric acid is a better solvent than nitric acid and is especially useful for the hydrolysis of non-orthophosphates.

## SAMPLES CONTAINING LARGE AMOUNTS OF ORGANIC MATTER

**Procedure (Nitric Perchloric Acid Digestion)**—Perchloric acid is an extremely useful reagent but its use can be hazardous unless certain precautions are observed. Never add perchloric acid to samples containing organic matter until after the easily oxidizable organic matter has been destroyed with nitric acid. Recommended reading: *Perchloric Acid Solutions* Chemical Safety Data Sheet SD11 (1947) Manufacturing Chemists Association 1825 Connecticut Ave NW Washington 9 D C.

To a sample (0.5 to 20 g) in a 250 ml Erlenmeyer flask add 30 ml of nitric acid. Boil gently to remove easily oxidizable organic matter (15 minutes is usually sufficient) cool slightly and add 10 to 20 ml of 70% perchloric acid. Boil

\* Association of Official Agricultural Chemists. Official Methods of Analysis 9th Ed. Sec 2018 1960.

\*\* Jacob K. D. and H. H. H. W. M. J. Assoc. Offic. Agr. Chemists 40 610-00 13

gently until the solution is colorless, or nearly so, and dense white fumes appear in the flask. Fume for 10 minutes, cool slightly, and add 50 ml. of water. Boil gently for a few minutes and cool. Dilute to volume in a volumetric flask, and filter through a dry filter.

This technique can be used for the decomposition of large amounts of paper in citrate-insoluble residues. The sample *must* be digested with nitric acid until the filter paper is destroyed before adding the perchloric acid.

### TOTAL PHOSPHORUS—ALKALIMETRIC AMMONIUM MOLYBDOPHOSPHATE METHOD <sup>29</sup>

Phosphorus in the form of orthophosphate is precipitated as ammonium molybdophosphate, which is filtered and dissolved in an excess of standard sodium hydroxide solution. The excess alkali is back-titrated with standard acid to a phenolphthalein end point.

The alkalimetric method is a good routine method; it will yield acceptable results in the hands of a careful worker. Details must be observed closely, however, if the method is to be of maximum value.

Sulfates lead to high results, so decomposition methods employing sulfuric acid should be avoided. Heating of the solution hastens precipitation but also causes the precipitation of extra molybdic oxide. As the precipitate is formed in a strongly acid medium, residual acid must be removed. Prolonged washing, on the other hand, causes some decomposition of the precipitate.

Even when used properly, the method yields slightly high results because the equivalence point of the titration is at a lower pH than the colorimetric end point. Titration to the pink side of the phenolphthalein end point yields even higher results.

**Reagents.** Molybdate Solution.—Dissolve 100 g. of molybdic anhydride ( $\text{MoO}_3$ ) or 118 g. of 85% molybdic acid in a mixture of 145 ml. of ammonium hydroxide and 270 ml. of water. Slowly stir the cooled solution into a mixture of 600 ml. nitric acid with 1150 ml. of water. Keep the solution in a warm place for several days, then decant it from any precipitate. Filter the solution through an inorganic filter just before using.

Ammonium Nitrate.—20% weight/volume.

Sodium Hydroxide.—0.3240 N (1 ml.  $\approx$  1 mg.  $\text{P}_2\text{O}_5$ ).

Nitric Acid.—0.3240 N.

Phenolphthalein.—Dissolve 1 g. in 100 ml. of 95% ethanol.

**Procedure.**—Dissolve a sample of fertilizer by one of the three methods described in the preceding section. Transfer an aliquot containing 10 to 40 mg. of  $\text{P}_2\text{O}_5$  to a 500-ml. wide-mouthed Erlenmeyer flask. Add 2 drops of methyl orange indicator, and add ammonium hydroxide dropwise until a precipitate forms or the indicator turns yellow. Add nitric acid dropwise until the precipitate dissolves or the indicator turns red. Add 50 ml. of ammonium nitrate solution. With the temperature in the range 25° to 30°C., add 50 ml. of ammonium molybdate solution with vigorous shaking (dropwise for the first 5 ml., then in a small stream). The ammonium molybdate solution should be free of precipitate, and the dispensing buret should be cleaned daily. Place the flask on a mechanical shaker for 30 minutes.

Decant *at once* through a pad of filter pulp. Transfer the precipitate to the

<sup>29</sup> Association of Official Agricultural Chemists, *Official Methods of Analysis*, 9th Ed., Secs. 2.017, 2.020, 2.021(a), 2.022(a), 1960.

filter with a jet of cold water. Wash the flask 3 times with small portions of cold water then wash the precipitate on the pad with cold water until free of acid (usually 10 times is sufficient). Transfer the precipitate and pad back to the wide mouthed flask and break up the pad with 50 ml of cold water. Dissolve the precipitate in standard alkali adding not more than a 3 ml excess. Add 6 drops of phenolphthalein indicator and titrate with standard acid to the disappearance of the pink color.

Calculation—When 0.3240 N NaOH and  $\text{HNO}_3$  are used 1 ml NaOH  $\approx$  1 mg P<sub>2</sub>O<sub>5</sub> and

$$\text{P}_2\text{O}_5 \text{ per cent} = \frac{\text{milliliters NaOH} - \text{milliliters HNO}_3}{10 \times \text{weight of sample grams}}$$

### TOTAL PHOSPHORUS—DIFFERENTIAL SPECTROPHOTOMETRIC METHOD<sup>30, 31, 32</sup>

A dilute solution of orthophosphate is treated with an acidified molybdovanadate reagent to form the colored molybdovanadophosphoric acid complex. Concurrently the color is developed in a solution containing a known amount of phosphorus. The standard is adjusted to read zero absorbance. The absorbance of the unknown is measured and the concentration is determined from a calibration curve or is calculated.

Although the molybdovanadophosphate color reaction is remarkably free of interferences certain precautions are in order. Oxides of nitrogen interfere and must be eliminated before the color is developed. Partially decomposed organic matter may interfere because of its color or through reduction of molybdenum. Iron in high concentrations as from basic slag causes high results. Silicates also may cause high results.

These difficulties are largely eliminated when perchloric acid is used in preparing solutions for analysis. Oxides of nitrogen and residual organic matter from nitric acid digestions are removed by evaporating to fumes of perchloric acid. Silicates are dehydrated and iron salts are converted to the perchlorate which absorbs less light.

The reaction is sensitive to variations in acidity and care must be taken to hold the acidity within prescribed limits. As heat intensifies the color sample and standard must be at the same temperature when the absorbance is measured.

**Apparatus**—Spectrophotometer with stray light filter and matched 1 cm absorption cells. The instrument should also be fitted with a liquid cooled lamp housing.

**Reagents** Molybdovanadate—Dissolve 40 g of ammonium molybdate tetrahydrate in 400 ml of hot water. Dissolve 2 g of ammonium metavanadate in 250 ml of hot water cool and add 450 ml of 70% perchloric acid. Gradually add the molybdate solution to the vanadate solution at room temperature with stirring and dilute to 2 l.

**Standard Phosphate Solution**—Obtain a sample of highest purity potassium dihydrogen phosphate of certified composition. Prepare a series of solutions con-

<sup>30</sup> Association of Official Agricultural Chemists Official Methods of Analysis 9th Ed Secs 2023, 2024, 2025, 2026, 2027, 1960.

<sup>31</sup> Brabson J. A. Dunn R. L. Epps E. A. Jr. Hoffman W. M. and Jacob K. D. J. Assoc. Off. Agr. Chemists 41, 517-24, 1958.

<sup>32</sup> Cee A. and Deitz V. R. Anal. Chem. 25, 1320-21, 1953.

taining from 0.4 to 1.0 mg. of  $P_2O_5$  per ml. in 0.1 mg. increments. These solutions are used for preparation of the calibration curve. Prepare fresh solutions containing 0.4 and 0.6 mg. of  $P_2O_5$  per ml. at weekly intervals for checking the calibration curve.

**Calibration Curve.**—Transfer 5-ml. aliquots of the standard solutions by means of matched pipets to a series of seven calibrated 100-ml. volumetric flasks and dilute to about 50 ml. Add 20 ml. of molybdovanadate reagent to all the solutions within a 5-minute period. Dilute to the mark, mix thoroughly, and let stand for 10 minutes for color development.

Fill two absorption cells with the standard containing 2 mg. of  $P_2O_5$ , and place the cells in the photometer. Set the wavelength at 400  $m\mu$ , and adjust the slit width so that the absorbance of one of the solutions reads zero. Check the absorbance of the second solution. If exact matching occurs or if a positive reading is obtained, use the cells in the order read, with the first cell designated as the standard cell and the second as the sample cell. Otherwise, reverse the order of the cells and readjust the slit so that the solution in the first cell has zero absorbance. If the sample cell has an absorbance greater than 0.001, correct subsequent absorbance readings by subtracting the amount found. Determine the absorbance of the other solutions with the instrument set at zero absorbance for the 2-mg. standard. Empty and refill the standard cell with the 2-mg. standard after each determination to avoid errors arising from temperature changes. Plot absorbance against concentration of  $P_2O_5$ .

**Check on Comparison Standard.**—An inherent weakness of the differential spectrophotometric method is that an error in the standard containing 2.0 mg.  $P_2O_5$  will affect all determinations made against this standard. The likelihood of error is greatly reduced by preparing a second standard as a check on the first. The following procedure should be used with each set of determinations requiring the preparation of a new comparison standard.

Transfer 5-ml. aliquots of standard solutions containing 2.0 and 3.0 mg. of  $P_2O_5$  to 100-ml. volumetric flasks and develop the color as in the preparation of the calibration curve. Adjust the instrument to read zero absorbance for the 2-mg. standard. Determine the absorbance for the 3-mg. standard; the absorbance of this solution must agree closely with the result on the standard curve. Otherwise, prepare fresh solutions of potassium dihydrogen phosphate and repeat the determinations.

**Procedure.**—Digest a 1-g. sample with a mixture of 25 ml. of nitric acid and 15 ml. of perchloric acid. If the sample contains, or is suspected of containing, a high proportion of organic matter, digest it first with nitric acid and then complete the digestion with the acid mixture. Evaporate to fumes of perchloric acid and fume for 3 minutes to remove oxides of nitrogen. Dilute to 50 ml. and boil for 2 minutes to remove decomposition products of perchloric acid. Filter (if necessary), cool, and dilute to volume in a volumetric flask. If the sample contains less than 5%  $P_2O_5$ , dilute to 250 ml. For higher concentrations of phosphate, dilute to such a volume that a 5- or 10-ml. aliquot contains 2 to 5 mg. of  $P_2O_5$ .

For samples containing less than 5%  $P_2O_5$ , transfer a 5-ml. aliquot to a 100-ml. volumetric flask and add 5 ml. of the standard phosphate solution containing 2 mg. of  $P_2O_5$ . Use an aliquot containing 2 to 5 mg. of  $P_2O_5$  for samples containing more than 5%  $P_2O_5$ .

Develop the color simultaneously in the unknown and in the respective standards containing 2 and 3 mg of  $P_2O_5$ . Check the absorbance of the 3 mg standard against that of the 2 mg standard, then proceed with the analysis as described in connection with the calibration curve. Empty and refill the cell containing the 2 mg standard after each determination to compensate for temperature differences.

Calculation—

$$P_2O_5, \text{ per cent} = \frac{\text{milligrams } P_2O_5 \text{ in aliquot}}{\text{milligrams sample in aliquot}} \times 100$$

### TOTAL PHOSPHORUS—ALKALIMETRIC QUINOLINIUM MOLYBDOPHOSPHATE METHOD<sup>33, 34</sup>

Phosphorus as orthophosphate is separated as quinolinium molybdophosphate from a boiling solution in the presence of citrate. The salt is separated and dissolved in an excess of standard alkali. The excess alkali is back titrated in the presence of a thymol blue phenolphthalein indicator.

Superficially, the quinolinium method appears to be closely similar to the alkalimetric ammonium molybdophosphate method but actually it is quite different. Molybdophosphoric acid is formed first in the presence of citrate. The base quinoline then is added to form crystals of quinolinium molybdophosphate.

The citrate in the reagent complexes ammonium ion, thus preventing interference from precipitation of ammonium molybdophosphate by the ammonium salts usually present in mixed fertilizers. Large quantities of ammonium salts must be avoided, however, as they may cause formation of a mixed precipitate. The citrate also lessens interference from soluble silica. When a large amount of silica is involved it should be dehydrated with perchloric acid and removed by filtration.

**Reagents** Citric Acid-Molybdate Solution—Add 54 g of molybdic anhydride ( $MoO_3$ ) to 200 ml of water in a metal or plastic dish. Avoid molybdic acid<sup>35</sup> which is largely ammonium molybdate. Stirring continuously add 11 g of reagent grade sodium hydroxide pellets. Continue the stirring and heat the suspension until virtually all the molybdic anhydride is dissolved. Dissolve 60 g of citric acid in 250 to 300 ml of water and add 140 ml of hydrochloric acid. Stir the molybdate solution into the acid solution. Cool, filter through a pulp pad to remove turbidity and dilute to 1 liter. A slight coloration of the reagent is normal should the color be dark blue or green, discharge most of it by dropwise addition of a dilute (0.5 to 1%) solution of potassium bromate. Transfer to a polyethylene bottle and store in the dark.

**Quinoline Solution**—Add 60 ml of hydrochloric acid to 400 ml of water in a 1 liter beaker and heat to 80°C. Stir in 50 ml of high purity synthetic quinoline. When the quinoline has dissolved, dilute the solution to 1 liter and filter through a pulp pad. Store in a polyethylene bottle. The quinoline must be entirely free of reducing agents.

Quinoline can be freed of impurities by dissolving it in hydrochloric acid and adding an excess of zinc chloride in dilute hydrochloric acid solution to precipitate a double salt of quinolinium hydrochloride with zinc chloride. The salt is filtered on an inorganic filter and washed with dilute hydrochloric acid. The

<sup>33</sup> Wilson, H. N., *Analyst*, **76**, 65-76, 1951.

<sup>34</sup> Wilson, H. N., *ibid.*, **79**, 535-46, 1954.



quinoline is then regenerated with an excess of sodium hydroxide, dried, and distilled.

**Indicator.**—Mix 3 volumes of 0.1% thymol blue solution with 2 of phenolphthalein solution. To prepare the thymol blue solution, add 2.2 ml. of 0.1 *N* NaOH to 0.1 g. of thymol blue and dilute to 100 ml. with 50% ethanol. Dissolve 0.1 g. of phenolphthalein in 100 ml. of 50% ethanol.

**Sodium Hydroxide.**—0.5 *N*, 1 ml.  $\approx$  1.366 mg.  $P_2O_5$ .

**Hydrochloric Acid.**—0.5 *N*.

**Sodium Hydroxide.**—0.1 *N*.

**Hydrochloric Acid.**—0.1 *N*.

**Procedure.**—Dissolve a sample by one of the three methods described. Digestion with nitric and hydrochloric acids will remove most of the ammonia. The nitric-perchloric acid method is advantageous when silica needs to be dehydrated or when organic matter is present.

Transfer an aliquot containing 20 to 50 mg. of  $P_2O_5$  to a 500-ml. wide-mouthed Erlenmeyer flask which has been marked at 150 ml. When the sample does not contain calcium, dissolve 100 to 200 mg. of phosphorus-free calcium carbonate in the solution. Heat the solution nearly to boiling and add, dropwise, 20% sodium hydroxide solution until a faint precipitate persists. (The sodium hydroxide should be prepared in a metal beaker, but stored and dispensed from a plastic container.) Bring the solution to a boil and add hydrochloric acid, dropwise, to dissolve the precipitate.

Dilute the solution to 150 ml., add 50 ml. of the citric acid-molybdate solution, and boil gently for 3 minutes. The solution must be free of precipitate at this point. Should precipitation occur, contamination of the reagents or the solution with ammonia should be suspected.

Add 25 ml. of the quinoline reagent, dropwise at first, then in a slow stream, swirling the solution during the addition to ensure a coarsely crystalline precipitate. Place the flask in boiling water for 5 minutes, then cool to room temperature in running water.

Decant through a pad of filter pulp. Transfer the precipitate to the filter with a jet of cold water. Wash the flask with small portions of cold water, then wash the precipitate free of acid. Transfer the pad to the precipitation flask and break it up with about 50 ml. of water. Dissolve the precipitate in an excess of 0.5 *N* sodium hydroxide. Shake the slurry and examine it to ensure the absence of undissolved particles. Add 0.5 to 1.0 ml. of the thymol blue-phenolphthalein indicator and back-titrate with 0.5 *N* hydrochloric acid. The color change is from violet to greenish blue and finally to yellow at the end point.

Run a blank on all the reagents. Use 0.1 *N* base and acid for the titration, and calculate the net base used to 0.5 *N* NaOH. Subtract this blank from the 0.5 *N* NaOH used in neutralizing the original precipitate.

**Calculation.**—

1 ml. of 0.5 *N* NaOH  $\approx$  1.366 mg.  $P_2O_5$

$$P_2O_5, \text{ per cent} = \frac{\text{milliliters of NaOH} \times 1.366}{10 \times \text{weight sample, grams}}$$

# TOTAL PHOSPHORUS—GRAVIMETRIC QUINOLINIUM MOLYBDOPHOSPHATE METHOD <sup>35 36</sup>

Phosphorus is precipitated in the same way as in the alkalimetric quinolinium method. The precipitate is filtered on a glass fiber filter, dried at 250°C., and weighed as the anhydrous quinolinium salt,  $3C_9H_7N \cdot H_3PMo_{12}O_{40}$ .

With attention to detail precipitates of essentially theoretical composition are obtained and the method yields quite accurate results. A high molecular weight and a low phosphorus content make the quinolinium salt an excellent weighing form for phosphorus.

**Reagents Citric Acid Molybdate Solution**—Prepare as for alkalimetric quinolinium method.

**Quinoline Solution**—Prepare as for alkalimetric quinolinium method.

**Procedure**—Dissolve the sample by one of the three methods described. Ammonium salts and silicates in significant quantities can cause difficulty, so care must be taken to introduce neither in the reagents.

Pipet an aliquot containing not more than 25 mg. of  $P_2O_5$  into a 500 ml. wide mouthed Erlenmeyer flask. Add 100 ml. of water, then 25 ml. of the citric acid molybdate solution. Boil gently for 3 minutes. The solution must be clear at this point; a precipitate indicates contamination with ammonia. Add 125 ml. of the quinoline solution from a buret, dropwise for the first few milliliters then in a slow stream. Swirl the solution during the addition to promote growth of crystals. Allow to stand for 5 minutes with occasional swirling, to coagulate the precipitate. Cool to room temperature in running water.

Place a 2.4 cm. circle of glass fiber filter paper in a Gooch crucible (Coors No. 4 or equivalent), apply suction, and wash a few times with distilled water. Dry at 250°C. Cool in a desiccator and weigh.

Filter the solution through the tared crucible; transfer the precipitate to the crucible with a minimum of water, and wash the precipitate twice with 5 ml. portions of water. Dry to constant weight (about 15 minutes) in a forced draft oven at 250°C., and cool to room temperature over freshly dried activated alumina in an evacuated desiccator. Subtract a reagent blank as determined on the current batch of reagents.

**Calculation**—

$$P_2O_5, \text{ per cent} = \frac{\text{net weight of precipitate, milligrams} \times 3.2074}{\text{milligrams sample analyzed}}$$

## WATER SOLUBLE PHOSPHORUS <sup>37 38</sup>

The water solubility of the phosphorus in a fertilizer is useful as a guide in manufacturing and in checking for compliance with specifications. The major phosphatic constituent in superphosphate, for example, is monocalcium phosphate which is water soluble. When a superphosphate is ammoniated, however, the

<sup>35</sup> Perrin, C. H., *J. Assoc. Offic. Agr. Chemists*, **41**, 758-63, 1958.

<sup>36</sup> Wilson, H. N., *Analyst*, **79**, 535-46, 1954.

<sup>37</sup> Association of Official Agricultural Chemists, *Official Methods of Analysis*, 9th Ed., Secs. 2.028, 2.029, 1960.

<sup>38</sup> Brabson, J. A., Jacob, K. D., Withide, W. D., and Hoffman, W. M., *J. Assoc. Offic. Agr. Chemists*, **42**, 503-7, 1959.

water-solubility is decreased through formation of more basic calcium phosphates, and the water-soluble phosphates that remain are primarily ammonium salts.

Water-soluble compounds interfere in the determination of citrate-insoluble phosphorus in mixed fertilizers and acidulated materials. These fertilizers, therefore, are extracted with water prior to extraction with citrate, even though the water-soluble phosphorus may not be determined.

**Procedure.**—Place a 1-g. sample on a 9-cm. filter (Whatman No. 2 or equivalent) and wash with successive small portions of water until the volume of filtrate approaches 250 ml. Allow each portion of wash water to pass through the filter before adding another, and if, after 30 minutes, it is obvious that the washing cannot be completed in 1 hour, use light suction. If the filtrate is turbid, add 1 to 2 ml. of nitric acid, dilute to the mark, and mix well. Pipet a suitable aliquot and hydrolyze, if necessary, to the orthophosphate. Determine phosphorus by the alkalimetric method or by the differential spectrophotometric method, as described for total phosphorus. Reserve the filter and residue for the determination of citrate-insoluble phosphorus.

### CITRATE-INSOLUBLE PHOSPHORUS<sup>39</sup>

Phosphatic fertilizers usually contain some phosphorus that is insoluble in a neutral solution of ammonium citrate. This citrate-insoluble phosphate is taken as a measure of the phosphorus that will not be available to plants. Unreacted phosphate rock in a superphosphate, for example, is citrate-insoluble and is not readily utilized by plants.

The method is empirical. The residue from the determination of water-soluble phosphorus is extracted with citrate solution under prescribed conditions. Phosphorus in the residue from the citrate extraction is determined by the alkalimetric method or by the differential spectrophotometric method.

**Reagents.** **Neutral Ammonium Citrate.**—Dissolve 370 g. of citric acid in 1500 ml. of water and nearly neutralize with ammonium hydroxide (about 345 ml. of the usual reagent containing 28 to 30%  $\text{NH}_3$ ). When weaker ammonium hydroxide is used, use less water to dissolve the citric acid. Cool to 20°C. and adjust the pH to exactly 7.0 by small additions of ammonium hydroxide; a pH meter should be used. Then adjust the specific gravity to 1.09 at 20°C. Check the pH at weekly intervals and adjust as necessary.

The pH of the solution is critical. Colorimetric methods can be used in its adjustment but are much less reliable than electrometric methods. Even with electrometric methods, an independent check with a second pH meter is a wise precaution.

**Ammonium Nitrate.**—Dissolve 50 g. of  $\text{NH}_4\text{NO}_3$  in 1 liter of water. Add a few drops of methyl red, and just discharge the red color with dilute ammonium hydroxide.

**Citrate Extraction.** **Acidulated Materials and Mixed Fertilizers.**—Make the citrate digestion on the residue from the water-soluble determination within 1 hour after the water extraction. Transfer 100 ml. of neutral ammonium citrate solution to a 250-ml. rubber-stoppered volumetric flask ("fertilizer flask") or Erlenmeyer flask, and heat the flask and contents to 65°C. Add the residue and filter paper

<sup>39</sup> Association of Official Agricultural Chemists, Official Methods of Analysis, 9th Ed., Secs. 2.030, 2.031, 1960.

from the water extraction. Stopper the flask and shake vigorously to break up the paper. Relieve the pressure by loosening the stopper momentarily, then stopper tightly. Fasten the flask in an apparatus that will hold the temperature at 65°C and will so agitate the contents of the flask that dispersion of the sample in citrate solution is continually maintained and entire inner surface of flask and stopper is continually bathed with solution. —AOAC Digest for exactly 1 hour.

Quickly filter the extract through a Whatman No. 5 paper (or equivalent) or through a paper pulp pad with the aid of suction. Wash with water at 65°C until the filtrate reaches a volume of about 350 ml. Should the sample yield a cloudy filtrate repeat the determination and wash the pad with a 5% ammonium nitrate solution at 65°C.

**Nonacidulated Materials**—Place a 1 g sample on a 9 cm No. 2 Whatman filter paper or equivalent and without washing transfer sample and paper to a 250 ml fertilizer flask containing 100 ml of neutral ammonium citrate solution previously heated to 65°C. Proceed as directed for acidulated samples.

**Decomposition of Citrate Insoluble Residue**—Among the several ways of decomposing citrate insoluble residue a common practice is to digest it (and the paper) with nitric and hydrochloric acids in a fertilizer flask. The slurry is diluted to the mark and filtered on a dry filter prior to taking an aliquot for analysis. Use of a volumetric flask is a practical expedient in the analysis of citrate insoluble residues but its use for similar digestions in the decomposition of high analysis fertilizers is an indefensible practice.

Another convenient method is to transfer the paper and contents to an unglazed clay crucible (annealing cup) and to burn off the paper in a muffle furnace at the minimum temperature. The residue can be transferred to a beaker and dissolved in hydrochloric acid (preferably) nitric acid or perchloric acid. Removal of the paper permits use of the entire citrate insoluble residue for the phosphorus determination—a distinct advantage when the amount of citrate insoluble phosphorus is quite low.

Wetashing of the paper and citrate insoluble residue with a nitric perchloric acid mixture is another useful technique when the amount of phosphorus is quite low. This procedure is particularly advantageous when the sample contains organic phosphates from materials such as tankage or cottonseed meal.

**Determination Alkalimetric Method**—Transfer the solution (or an aliquot) obtained from one of the decomposition methods to a 500 ml wide mouthed Erlenmeyer flask and determine phosphorus by the alkalimetric method used for total phosphorus.

**Differential Spectrophotometric Method**—Preparation of the solution is more critical when the spectrophotometric method is to be used. The dryashing technique with subsequent digestion of the residue in perchloric acid is well suited for inorganic phosphates. Wetashing with nitric and finally with perchloric acid is applicable to all residues including those which contain organic phosphates.

The amount of acid in the sample should not exceed the equivalent of 2 ml of 70% perchloric acid. Since the solution must be filtered to remove the insoluble residue the best procedure is to add to an aliquot 20 mg of  $P_2O_5$  before developing the color.

DIRECT AVAILABILITY METHODS <sup>40, 41, 42, 43, 44, 45</sup>

Methods have been proposed for the direct determination of available phosphorus in the combined water and citrate extracts. These methods are being studied by AOAC, and it may be expected that a direct availability method will be adopted soon.

POTASSIUM <sup>46, 47, 48</sup>

Potassium or "potash" in fertilizers is usually added as the chloride, although some less soluble salts, such as the sulfate, are used occasionally.

Water solubility of the potassium is determined only on the pure salts. When they are blended with other ingredients, as in mixed fertilizers, the mixture is boiled with an ammonium oxalate or ammonium carbonate solution, and the filtrate from the digestion is analyzed for potassium. Total potassium is determined in organic materials such as cottonseed meal and tobacco stems.

The classical gravimetric method, in which potassium is weighed as the chloroplatinate, is an excellent procedure in experienced hands. However, it is time-consuming, it requires above-average technique, and it entails a considerable investment in platinum, so it will not be included in this chapter. The procedures described here are better suited for the laboratory that is called upon to analyze an occasional sample for potassium; they are also suitable for production analyses.

## TITRIMETRIC TETRAPHENYLBORATE METHOD

The titrimetric tetraphenylborate method for potassium in fertilizers requires a somewhat expensive reagent, sodium tetraphenylborate (STPB), but this cost is offset by a relatively small investment in equipment. The procedure is simple; it can be used by skilled technicians who may lack broad theoretical training.

Ammonium ions form an insoluble tetraphenylborate salt analogous to the potassium compound. Since fertilizers usually contain ammonium salts, and ammonium oxalate is used to prepare solutions of fertilizers, interference by ammonium ions is prevented by adding formaldehyde, which reacts to form hexamethylenetetramine. Other ions generally present in fertilizers do not interfere.

An aliquot of the water, ammonium oxalate, or acid extract of the fertilizer is made alkaline with sodium hydroxide, and formaldehyde is added. Potassium is precipitated with an excess of standard STPB solution. The excess STPB in an aliquot of the filtrate is titrated with standard quaternary ammonium chloride in the presence of Clayton yellow indicator.

*Apparatus.*—Use microburets for dispensing small volumes of standard solutions.

*Reagents.* Sodium Hydroxide.—Dissolve 20 g. of the reagent in 100 ml. of water.

Formaldehyde.—Reagent-grade, 37%.

<sup>40</sup> Allen, H. R., Swift, E., Hays, R., and Kaufman, Z. F., J. Assoc. Offic. Agr. Chemists, 35, 764–67, 1952.

<sup>41</sup> Brabson, J. A., and Wilhide, W. D., *Ibid.*, 42, 574–78, 1959.

<sup>42</sup> Gehrke, C. W., and Johnson, F. J., *Ibid.*, 42, 569–74, 1959.

<sup>43</sup> Hoffman, W. M., and Jacob, K. D., *Ibid.*, 42, 508–11, 1959.

<sup>44</sup> Perrin, C. H., *Ibid.*, 42, 567–68, 1959.

<sup>45</sup> Teague, R. T., Jr., *Ibid.*, 36, 880–85, 1953.

<sup>46</sup> Association of Official Agricultural Chemists, Official Methods of Analysis, 9th Ed., Secs. 2.073, 2.074, 2.075, 1960.

<sup>47</sup> Epps, E. M., and Burden, J. C., *Anal. Chem.*, 30, 1882–83, 1958.

<sup>48</sup> Schall, E. D., *Ibid.*, 29, 1044–46, 1957.

**Sodium Tetraphenylborate**—Dissolve 12 g of the reagent (source J T Baker Chemical Company Phillipsburg N J) in 800 ml of water. Add 20 to 25 g of aluminum hydroxide stir for 5 minutes and filter (Whatman No 42 paper or equivalent). Should the first portion of filtrate be cloudy collect it separately and refilter it. Add 2 ml of 20% sodium hydroxide to the clear filtrate dilute to 1 liter and mix thoroughly. Allow the solution to age for 2 days in a polyethylene container before standardization.

**Clayton Yellow Indicator**—Dissolve 0.040 g of Clayton yellow (Color Index No 19510) in 100 ml of water.

**Quaternary Ammonium Chloride**—Dilute 50 ml of 12.8% Zephiran chloride (Winthrop Stearns Inc New York 18 N Y or local pharmacies) to 1 liter. Determine the relation of this solution to the STPB solution as follows: to 100 ml of STPB solution in a 125 ml Erlenmeyer flask add 20 ml of water 1 ml of 20% sodium hydroxide 2.5 ml of formaldehyde 1.5 ml of 4% ammonium oxalate solution and 6 to 8 drops of indicator titrate with Zephiran chloride solution to the pink end point so dilute the Zephiran chloride that 2 ml of it is equivalent to 1 ml of STPB solution.

**Potassium Dihydrogen Phosphate**—Highest purity reagent of certified composition. Dry for 2 hours at 105°C before weighing.

**Standardization of Sodium Tetraphenylborate**—Prepare a standard solution of potassium by dissolving 2.500 g of potassium dihydrogen phosphate (34.61% K<sub>2</sub>O) in water adding 50 ml of 4% ammonium oxalate solution and diluting the mixture to volume in a 250 ml volumetric flask. To 15 ml of this solution in a 100 ml volumetric flask add 2 ml of 20% sodium hydroxide 5 ml of 37% formaldehyde and 43.0 ml of STPB solution. Dilute to volume with water and mix thoroughly. After 10 minutes filter through a dry filter. Transfer 50 ml of the filtrate to a 125 ml Erlenmeyer flask and add 6 to 8 drops of Clayton yellow indicator. Titrate the excess STPB solution with Zephiran chloride to a pink end point. Calculate the factor by the relation

$$F = \frac{34.61}{43 - \text{ml Zephiran}} = \% \text{ K}_2\text{O per milliliter of STPB solution}$$

Factor *F* applies whenever 2.5 g of sample is diluted to 250 ml and a 15 ml aliquot is used for the determination of potash.

**Preparation of Sample for Analysis** **Water Soluble Salts**—Dissolve 2.5 g of fertilizer (1.25 g when K<sub>2</sub>O content exceeds 50%) in water and dilute to 250 ml in a volumetric flask. In the event of an insoluble residue use the method specified for mixed fertilizers.

**Mixed Fertilizers**—Transfer 2.5 g of sample (1.25 g when K<sub>2</sub>O content exceeds 50%) to a 400 ml beaker and add 125 ml of water and 50 ml of saturated ammonium oxalate solution. Boil for 30 minutes. Foaming can be controlled by adding 1 ml of a diglycol stearate solution (20 g diglycol stearate technical in a mixture of 500 ml benzene and 500 ml 95% ethanol). Add a slight excess of ammonium hydroxide (test paper) and transfer to a 250 ml volumetric flask. Cool dilute to volume and filter through a dry filter to obtain a solution for analysis.

**Determination**—Transfer a 15 ml aliquot of the sample solution to a 100 ml volumetric flask. Add 2 ml of 20% sodium hydroxide and 5 ml of formaldehyde. Add 1 ml of STPB solution for each 1% K<sub>2</sub>O expected plus an 8 ml excess to ensure complete precipitation. Dilute to volume and after 10 minutes filter through a dry filter (Whatman No 12 or equivalent).

To a 50-ml. aliquot of the filtrate in a 125-ml. Erlenmeyer flask, add 6 to 8 drops of Clayton yellow indicator. Titrate with Zephiran chloride to the same pink end point used in the standardization.

Calculation.—For 2.5-g. sample,

$$\text{K}_2\text{O, per cent} = (\text{milliliters of STPB} - \text{milliliters of Zephiran}) \times F$$

For 1.25-g. sample,

$$\text{K}_2\text{O, per cent} = (\text{milliliters of STPB} - \text{milliliters of Zephiran}) \times 2F$$

Precautions.—Whereas an excess of STPB must be added to ensure complete precipitation and to depress the solubility of the precipitated potassium salt, a large excess obscures the end point of the back-titration in the presence of a large quantity of precipitate. When a very low back-titration is obtained, the determination should be repeated with a greater amount of precipitant.

Although the STPB solution is fairly stable after the initial aging step, it should be checked daily to make sure that it has not deteriorated.

Avoid the error of mixing alkali and formaldehyde and adding them as one reagent as after 1 day of standing the mixture will not complex ammonia.

#### FLAME PHOTOMETRIC METHOD—DIRECT INTENSITY <sup>49, 50, 51, 52</sup>

Flame photometers vary widely in their operating characteristics, and methods must be tailored to suit the instrument. Breakdowns occur, regardless of the make of instrument, and the availability of personnel capable of keeping the instrument in working order should be considered in deciding whether or not to buy a flame photometer or a flame attachment.

Potash is determined flame photometrically by direct intensity methods and by methods based upon the principle of an internal standard. Direct intensity methods are the more widely used, but the choice of method may depend upon the equipment available, and both types of procedure are described.

The direct intensity approach has the advantage that it may be used on any flame photometer, including instruments equipped for measurements with an internal standard. An aqueous solution of the sample is atomized into a flame, which causes potassium to emit its characteristic spectrum. The light is passed through a monochromator to isolate the stronger lines of potassium, and their intensity is measured with a photoelectric device. The results are evaluated by comparison with a calibration curve.

Some anions, particularly sulfate and phosphate, have a pronounced effect on the intensity of the emission. In the procedure described here, the anions in a solution of the sample are exchanged for nitrate ions on an anion exchange resin.

**Reagents.** Ammonium Carbonate.—Dissolve 50 g. of reagent-grade ammonium carbonate in 1 liter of water.

**Methyl Red Indicator.**—Dissolve 0.2 g. of the acid in 100 ml. of 95% ethanol.

**Nitric Acid.**—Dilute 1 volume of the reagent with 10 volumes of water.

<sup>49</sup> Association of Official Agricultural Chemists, *Official Methods of Analysis*, 9th Ed., Secs. 2.067, 2.068, 2.069, 2.070, 2.071, 2.072, 1960.

<sup>50</sup> Gardiner, K. W., *Physical Methods of Chemical Analysis*, Vol. III, Berl, W. G., ed., Academic Press Inc., New York, pp. 219–80, 1956.

<sup>51</sup> Gehrke, C. W., Afsprung, H. E., and Wood, E. L., *J. Agr. Food Chem.*, 3, 48–50, 1955.

<sup>52</sup> Gehrke, C. W., and Wood, E. L., *Missouri Univ. Agr. Expt. Sta., Research Bull.* 635, 1957.

**Potassium Nitrate or Chloride**—Recrystallize twice from water. Dry the nitrate at 105°C for 5 hours. Dry the chloride at 105°C for 1 hour then ignite it at 500°C for 1 hour.

**Anion Exchange Resin**—The availability of specific resins changes as newly developed resins supplant older ones. The following resins proved suitable when this method was studied collaboratively under sponsorship of AOAC. Amberlite IR 4B (Fisher Scientific Co. Pittsburgh Pa.) Duolite A7 or Duolite A41 (Rohm and Haas Co. Redwood City Calif.) Deacidite or Permutit S (Permutit Inc. New York N. Y.). Other resins of comparable characteristics should also be suitable.

The resin should be in the nitrate form when it is used for separation of interfering anions. The following procedure is designed to regenerate the used resin which must be done after it has been used 10 times. To about 1.5 lb of the resin in a 4 l beaker add sufficient 5% sodium hydroxide to float the resin when it is stirred. Stir for 30 minutes allow the resin to settle and decant the liquid treating the resin this way three times. Add about 3 liters of water stir a few minutes and decant wash this way five times to remove the excess sodium hydroxide.

To convert the resin to the nitrate form treat it three times with 5% nitric acid allowing the resin to settle each time and decanting the acid. Wash the resin by decantation or by backwashing in a column until the pH of the washings is above 9. Drain off excess water and store the moist resin in a closed container.

New resin may be received in the hydroxide form. Treat this resin only one time with 5% sodium hydroxide and proceed as directed above for the spent resin.

Prepare resin columns from 12 in lengths of standard wall glass tubing with an outside diameter of 2.5 cm. Connect one end of each tube to a 2 way stopcock by means of a rubber stopper or preferably by sealing the stopcock to the tubing. When a stopper is used choose one that leaves no void at the wall of the column and do not let the stopcock tubing protrude above the end of the stopper. Place a wad of glass wool over the outlet to the column open the stopcock and fill the column to a height of 8 inches with resin from a water suspension.

**Preparation of Calibration Curve**—Prepare a solution containing 1000 p.p.m. of potassium by dissolving 1.2929 g of potassium nitrate or 0.9584 g of potassium chloride in water and diluting to 500 ml. Then by dilution prepare solutions covering the range 0 to 80 p.p.m. of potassium at intervals of 10 p.p.m. or less. Adjust the flame photometer so that 50 p.p.m. of potassium gives a reading near midscale. Prepare a standard curve relating emission to concentration.

**Preparation of Sample for Analysis**—Potassium Chloride or Potassium Sulfate—Dissolve 1.5058 g of salt in water and dilute to 500 ml. The solution of potassium chloride is analyzed without further treatment. Potassium sulfate must be converted to the nitrate by passage through a resin column before analysis.

**Mixed Fertilizers and Potassium Magnesium Sulfate**—To 1.5058 g of sample in a 400 ml beaker add 100 ml of water and 20 ml of ammonium carbonate solution. Boil for 5 minutes. If the sample contains less than 30%  $K_2O$  transfer to a 250 ml volumetric flask cool and dilute to volume. Dilute the solution to 500 ml if the sample contains more than 30%  $K_2O$ . Filter the solution through a dry filter to obtain aliquots for analysis.

**Determination**—Put a 10 ml aliquot in a 250 ml beaker. Add a drop of methyl red indicator and neutralize to a pH of 5 by dropwise addition of dilute nitric acid. Add sufficient water to the column to just cover the resin then transfer the sample from the beaker to the column. Drain the column into a 250 ml volumetric flask at a rate of 2 drops per second. Rinse the beaker 3 times with water and add the washings to the column. Catch 75 ml of effluent and continue to add water so



that the resin will be covered as the stopcock is opened and an additional 100 ml. of washings is collected. Dilute to volume.

Atomize the solution under the same conditions used to prepare the standard curve. Check points on the standard curve at intervals to ensure proper calibration. Determine the parts per million of potassium in the sample from the standard curve.

**Calculation.**—For samples containing less than 30%  $K_2O$ ,

$$K_2O, \text{ per cent} = \text{p. p. m. } \frac{K}{2}$$

For samples containing more than 30%  $K_2O$ ,

$$K_2O, \text{ per cent} = \text{p. p. m. } K$$

**Independent Check on Performance of Instrument and Procedure.**—To 1.5058 g. of potassium acid phthalate and 0.5 g. of diammonium phosphate in a 400-ml. beaker, add 100 ml. of water and 20 ml. of ammonium carbonate solution. Proceed as directed for mixed fertilizers. The  $K_2O$  content of the sample is 23.0%.

#### FLAME PHOTOMETRIC METHOD—INTERNAL STANDARD <sup>53, 54, 55</sup>

A double-beam flame photometer is required for the internal standard technique. Another element, lithium, is added to the solution of the fertilizer before it is atomized. The intensity of the potassium emission is measured with one optical system and the emission of lithium with the other. Anions that affect the potassium emission similarly affect the emission of lithium, and since the ratio of the intensities of potassium and lithium is measured, the effect of anions is compensated.

The internal standard methods for determining potassium used in the author's laboratory, since 1952, have obviated the necessity for anion removal in determining potassium in fertilizers. The procedure described here has been used with Perkin-Elmer models 52-C and 146 flame photometers. Although the optimum strengths of solutions and ratios of lithium to potassium may differ somewhat for other instruments, the general principles should apply.

A solution of the sample, mixed with a fixed amount of lithium solution, is atomized in a propane flame. The light passes through a monochromator where it is dispersed into the spectrum of the alkalis and then to a beam-splitting mirror. One beam falls on a movable slit, adjusted to allow potassium light to pass, and the other falls on a fixed slit, set to allow only lithium light to pass.

The light strikes two phototubes, causing current to flow. The amplified signals are then balanced by a single potentiometer control. Since the lithium signal is made constant through the use of a fixed amount of lithium in samples and standards, the adjustment required to bring the potassium signal into balance is proportional to the potassium content of the unknown.

**Reagents.** Potassium Chloride.—Recrystallize twice from water, dry at 105°C., and heat for 1 hour at 500°C. Prepare a solution containing 0.5 p. p. m.  $K_2O$  by dissolving 1.5830 g. of the purified salt in water and diluting to 2 liters in a volumetric flask.

<sup>53</sup> Association of Official Agricultural Chemists, Official Methods of Analysis, 9th Ed., Secs. 2.060(a), 2.060(b), 1960.

<sup>54</sup> Berry, J. W., Chappell, D. G., and Barnes, R. B., Ind. Eng. Chem., Anal. Ed., 18, 19–24, 1946.

<sup>55</sup> Gardiner, K. W., Physical Methods of Chemical Analysis, Vol. III, Berl, W. G., ed., Academic Press Inc., New York, pp. 219–80, 1956.

**Lithium Chloride**—Dissolve 5 lb of the reagent in 2 to 3 liters of water. Allow to stand for 2 days, then filter through a fine fritted glass filter. Add 232 ml of 70% perchloric acid and dilute to 23,200 ml. This solution contains 16,000 p p m of lithium.

**Preparation of Calibration Curve**—Transfer 25 ml portions of the lithium solution to a series of eleven 500 ml volumetric flasks. Add 5 to 50 ml of potassium solution (in 5 ml increments) to ten of the flasks, and reserve the other as a zero standard. These solutions when diluted to volume, contain 0 to 50 p p m  $K_2O$ .

Perform the preliminary manipulations such as adjusting gas and air pressures and warming up the instrument according to the manufacturer's directions. Atomize the zero potassium standard. Set the internal standard dial at zero and adjust the meter needle to 50 by means of the gain controls. Then set the internal standard dial at 100 and atomize the 50 p p m  $K_2O$  standard. Again adjust the gain controls until the meter reads 50. Again atomize the zero and 50 p p m  $K_2O$  solutions and adjust the gain controls to bring the meter back to the null point. Repeat until steady readings are obtained, then atomize the other solutions and record the dial settings. Check the zero and 50 p p m  $K_2O$  settings again adjusting the gain controls if necessary, then obtain another set of readings for the other standards. Plot the internal standard dial readings against concentrations to obtain a calibration curve.

**Preparation of Samples for Analysis**—Use any of the applicable procedures described for water soluble salts or mixed fertilizers in the discussion of the volumetric method for potassium.

**Determination**—To an aliquot containing 10 to 15 mg of  $K_2O$  in a 500 ml volumetric flask, add 25 ml of the lithium chloride solution used in preparing the calibration standards. Dilute to volume.

With the instrument calibrated, atomize the sample solution and calculate the approximate  $K_2O$  content of the sample. Then atomize a standard which has nearly the same  $K_2O$  content. The internal standard dial reading should be the same as the one obtained in the original calibration; if not, stable conditions have not been reached, and the determination must be delayed until adjustments are made. Repeat the readings and take an average to obtain greater accuracy. Determine milligrams of  $K_2O$  from the calibration curve.

**Calculation.**—

$$K_2O, \text{ per cent} = \frac{\text{milligrams of } K_2O \text{ in aliquot} \times 100}{\text{milligrams of sample in aliquot}}$$

## ACID- OR BASE-FORMING QUALITY <sup>56 57 58 59 60 61 62</sup>

Fertilizers undergo reactions in the soil that may change the soil pH. The residues from ammonium salts, for example, increase the acidity of the soil, whereas the residue from calcium cyanamide decreases it.

<sup>56</sup> Allen, H. R., and Gault, L. J. *Assoc. Offic. Agr. Chemists* 26, 68-74, 1943.

<sup>57</sup> Association of Official Agricultural Chemists, *Official Methods of Analysis*, 9th Ed., Secs. 2 099, 2 100, 1960.

<sup>58</sup> Pierre, W. H. *Ind. Eng. Chem., Anal. Ed.*, 5, 229-34, 1933.

<sup>59</sup> Pierre, W. H. *J. Assoc. Offic. Agr. Chemists* 17, 101-7, 1931.

<sup>60</sup> Pierre, W. H., Tully, N., and Ashburn, H. V. *Ind. Eng. Chem., Anal. Ed.*, 10, 72-76, 1938.

<sup>61</sup> Smith, J. B. *J. Assoc. Offic. Agr. Chemists* 19, 284-88, 1936.

<sup>62</sup> Willis, L. G. *Ibid.*, 19, 509-12, 1936.

The acid- and base-forming qualities of specific compounds can be calculated. Exact knowledge of the formulation or the complete chemical composition of a fertilizer is required, however, to make these calculations. The method described here requires a minimum of analytical information to obtain an estimate of the acid- or base-forming characteristics of the fertilizer.

The following concepts provide a basis for determining the acid-base balance of a fertilizer.

- (a) Only one hydrogen of phosphoric acid is acid-forming. Monocalcium phosphate is considered a neutral salt; it has been shown to have little effect on the pH of most soils.
- (b) One-half of the nitrogen is acid-forming. All nitrogen compounds may be converted, through nitrification, to nitric acid and so neutralize bases in the soil. Experiments have shown, however, that plants take up twice as much nitrate as base from a nitrate salt, thus leaving half of the base for neutralization of acidity in the soil.
- (c) Sulfur and chlorine are acid-forming elements.
- (d) Calcium, magnesium, sodium, and potassium are base-forming elements.

Determination of the acid- or base-forming quality of a fertilizer involves calculation of the acidifying power of the nitrogen and measurement of the residual acidity or alkalinity of the non-nitrogen portion.

To measure this residual effect, a sample of the fertilizer is ignited at fairly low temperature with sodium carbonate and carbon black. Nitrogen compounds are decomposed, and the nitrogen is expelled. Chlorides, sulfates, and phosphates not combined with bases in the fertilizer react with equivalent portions of the sodium carbonate. The resultant sinter is treated with an excess of standard acid, and the excess acid is back-titrated.

*Reagents.* Sodium Carbonate.—2 *N*.

Hydrochloric Acid.—1 *N*.

Sodium Hydroxide.—0.5 *N*.

*Mixed Indicator.*—To 0.1 g. of bromocresol green and 0.02 g. of methyl orange in an agate mortar, slowly add 2 ml. of 0.1 *N* NaOH. Rub the solids until they dissolve. Dilute to 100 ml. with water.

Carbon Black.

*Procedure.*—Transfer an appropriate weight of sample to a 150-ml. borosilicate glass beaker. When the total plant-food content (total N + available  $P_2O_5$  + oxalate-soluble  $K_2O$ ) is less than 30%, use 1 g. of sample. Use 0.5 g. for higher-analysis materials, 0.25 g. for straight sodium nitrate or potassium nitrate. Add 10 ml. of 2 *N* sodium carbonate solution from a buret or pipet, then add 0.25 g. of carbon black and mix thoroughly. Place the beaker in a sand bath to the depth of the mixture and evaporate to dryness. An ashless filter paper cone, folded so that the base just fits into the beaker, will control spattering. The apex of the cone is cut off to form a 3-mm.-vent.

Place the beaker in a muffle furnace at 250°C. Raise the temperature gradually to the range 575° to 600°C., and hold it at this level for 1 hour. (All carbon need not be removed by the ignition.) Cool the beaker below 100°C., add 50 ml. of water, cover with a watch glass, and add 30 ml. of 1 *N* hydrochloric acid through the lip. When effervescence ceases, place the covered beaker on a steam bath or hot plate and hold the temperature just below boiling for 1 hour.

Filter through a paper pad in a Gooch crucible or a funnel and into a 250 ml filtering flask. Wash 5 times with 5 ml portions of hot water. Add 0.4 ml of the mixed indicator to the clear filtrate and titrate to a light green end point with 0.5 N sodium hydroxide. The proper end point is at pH 4.3 where green predominates over yellow.

**Blank Determination**—Dilute 10 ml of the 2 N sodium carbonate solution to 70 ml in a 250 ml Erlenmeyer flask. Carefully add 30 ml of 1 N hydrochloric acid. When effervescence ceases boil gently to remove carbon dioxide. Add mixed indicator and titrate with 0.5 N sodium hydroxide as described above. The volume of sodium hydroxide solution required for the titration is the blank.

**Calculations**—Mixed fertilizers usually but not always contain both acid forming and base forming constituents. The algebraic sum of these constituents determines whether a fertilizer is acid or base forming. By convention acid formers are given a negative sign and base formers a positive sign. The amounts are expressed in pounds of calcium carbonate per ton of fertilizer.

Nitrogen determined separately is always acid forming. Theoretically the nitric acid produced by the nitrification of 28 lb of nitrogen would require 100 lb of calcium carbonate for neutralization but actually only 50 lb of  $\text{CaCO}_3$  is required. In 1 ton of fertilizer 28 lb of nitrogen equals 1.4% N. It follows that 35.7 lb of  $\text{CaCO}_3$  is needed to neutralize the acid produced by 1 ton of fertilizer containing 1% nitrogen. The result is given a negative sign.

The non-nitrogen residue of the fertilizer can be either acid or base forming. When more alkali is required to titrate the residue than the blank, the residue is acid forming and the result is given a negative sign. When less alkali is required the fertilizer is base forming and the result is given a positive sign. The 0.5 N NaOH is equivalent to 0.025 g  $\text{CaCO}_3$  per ml. When a 1 g sample is used 1 ml of NaOH is equivalent to 0.025 g  $\text{CaCO}_3$  per g of sample, or 50 lb  $\text{CaCO}_3$  per ton of fertilizer.

When fertilizers contain citrate insoluble  $\text{P}_2\text{O}_5$ , a correction is applied. The citrate insoluble residue usually contains some phosphate rock that appears as a base forming material in the titration. Raw phosphate rock has little effect on the pH of any except the most acid soils. The correction is made on the assumption that the citrate insoluble residue is tricalcium phosphate, which supplies 3 moles of excess calcium per mole of  $\text{P}_2\text{O}_5$ . (Phosphate rock is not tricalcium phosphate, but the error introduced by the faulty assumption is small.) The correction (citrate insoluble  $\text{P}_2\text{O}_5 \times 28.2$ ) is also in terms of calcium carbonate per ton of fertilizer and is given a negative sign.

The acid base balance of the ash and the corrections for nitrogen and for citrate insoluble  $\text{P}_2\text{O}_5$  usually yield a negative algebraic sum which indicates that the fertilizer is acid forming. Only when the base forming capacity of the ash exceeds the acid forming capacity of the nitrogen plus the correction for citrate insoluble  $\text{P}_2\text{O}_5$  can a fertilizer be base forming.

**Calculations**—

$$\text{Total N} \times 35.7 = \text{lb } \text{CaCO}_3 \text{ ton (minus sign)}$$

$$\text{C I } \text{P}_2\text{O}_5 \times 28.2 = \text{lb } \text{CaCO}_3 \text{ ton (minus sign)}$$

$$\frac{\text{NaOH(blank)} - \text{NaOH(determination)}}{\text{wt sample, g}} \times 50 = \text{lb } \text{CaCO}_3 \text{ ton (plus or minus sign)}$$

## Chapter 35

# FUEL GASES AND RELATED PRODUCTS

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### INTRODUCTION AND SCOPE

Although the practice of gas analysis has undergone extensive changes, the techniques of taking samples and handling them during analysis seem to have taken, because of the fugitive nature of gas, a much longer time to assume a perfected or "standardized" form than has been the case with solid or liquid analysis. Many of the old forms of equipment have been superseded in modern practice, and with the rapidly expanding development of reliable instrumental analysis, as used in mass-spectrographic, infrared, and chromatographic procedures, there are already signs that currently useful "standard" equipment and procedures may soon be displaced. Modern needs in industry hardly permit the slower methods, and automatic equipment is rapidly displacing the individual analyst.

In the light of these observations, only those analytical procedures are described in this chapter which may be considered currently modern standard practice. They have achieved this status by continued use in the fuel gas industry, by recognition by regulatory bodies as reliable methods, or by formal acceptance and designation as standard methods by such organizations as the American Society for Testing and Materials and the American Standards Association. Many older, once familiar methods, such as Hempel, Elliott, Morehead, Shepherd-Porter, will not be found here.

An effort is made to include, as far as possible, descriptions of the methods and the principles on which the newer instruments operate, but detailed descriptions of their manipulation cannot be included because of the variety of manufacturers and models, as for example in the field of mass-spectrometers and gas chromatographic apparatus. Analysts using these instruments are to be referred to the respective operating manuals.

### SAMPLING

Samples of gas taken for analysis, as with other materials, must be "representative" of the large quantity of gas to which the analysis pertains. It is sometimes more difficult, however, to be certain of this than with solids and liquids, and greater care is often required in obtaining the sample. Precautions must be taken to avoid loss of any components, and to prevent contamination by other materials in the sample lines and confining equipment. Experience is the best guide in selecting

and using a sampling technique appropriate to any particular situation. A summary of some general aspects of sampling gases may, however, serve as useful guide posts.

**Size and Type of Sample**—The size of the sample must be adequate to give results of the best precision attainable with the instrument or procedure to be used for the analysis. Sometimes however the sample size is determined by the source of the sample or its method of collection. Samples for mass spectrometric determinations, or those of gases dissolved in solids or liquids, may be a few milliliter or microliters in size, while samples used in low temperature distillation analyses or for calorific value measurements may be many cubic feet in volume. Determination of trace constituents often requires a much larger sample than that to be used for estimating major constituents only.

Recommended sample volumes to provide for purging and for duplicate analyses and other tests if desired, are <sup>1 2</sup>

For chemical analyses	250-1000 cu. cm
For specific gravity with balance type instruments	1 cu. ft.
For heating value determination	3-5 cu. ft.
For hydrogen sulfide (Tutwiler method)	250-700 cu. cm
For hydrogen sulfide (cadmium sulfate method)	5 cu. ft.
For total sulfur (or organic sulfur)	10 cu. ft.
For fractionation analysis	5-10 cu. ft.
For ammonia determination (manufactured gas)	10 cu. ft.
For gasoline content (natural gas)	5-10 cu. ft.

A *continuous* cumulative or average sample is taken over a period of time if a time average value of the composition of a flowing stream of gas is required. A sample approximating a continuous sample may be obtained by combining instantaneous samples taken periodically through the time interval. The latter may be termed *intermittent* sampling.

An *instantaneous*, *grab*, or *snap* sample is taken over a very short period of time a few seconds to a minute or two, representing the composition of the gas at a particular time and place.

**Sample Containers**—The practical size of a sample container is determined of course, by the size of the sample to be collected but must be easily handled, stored and transported as the situation requires. General purpose containers for samples at atmospheric pressure are glass bulbs, closed with two stopcocks, having capacities of 150 to 300 ml. For gases under pressure metal containers are invariably used. If samples are to be shipped under pressure the containers must comply with requirements of the Interstate Commerce Commission as to construction and marking.

Sample containers for natural gas, manufactured gas, and liquefied petroleum gases to be analyzed by standard methods of the American Society for Testing and Materials are usually prescribed in the appropriate ASTM Standards. The variety available is illustrated in part in Fig. 35.1<sup>1 2 3</sup>. In Fig. 35.2, two of many arrangements of equipment for collecting samples at atmospheric pressure are shown.<sup>2</sup>

<sup>1</sup> Standard Method of Sampling Natural Gas, D1145-53, ASTM Standards Part 8, American Society for Testing and Materials, Philadelphia, Pa., p. 1248, 1958.

<sup>2</sup> Standard Method of Sampling Manufactured Gas, D1247-54, ASTM Standards Part 8, American Society for Testing and Materials, Philadelphia, Pa., p. 1261, 1958.

<sup>3</sup> Standard Method of Sampling Liquefied Petroleum Gases, D1265-55, ASTM Standards, Part 8, American Society for Testing and Materials, Philadelphia, Pa., p. 1275, 1954.

Materials from which containers are fabricated must not react with any constituent of the sample. Glass, quartz, stainless steel are the least affected and

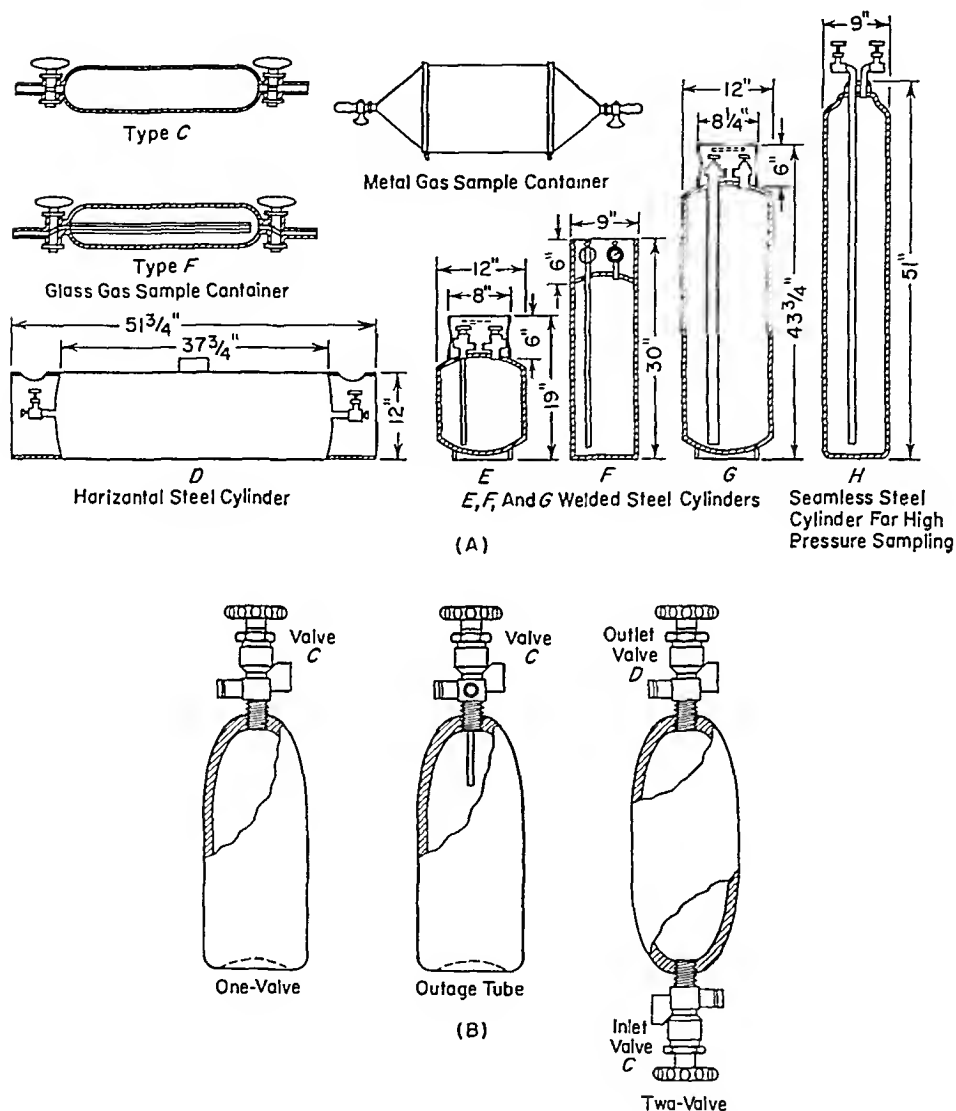


FIG. 35-1. Sample Containers: (A) for Natural and Manufactured Gases; (B) for Liquefied Petroleum Gases. (Reproduced with permission from ASTM Standards, ASTM, Philadelphia, 1958.)

most widely used. Brass, copper, and steel are often satisfactory in the absence of sulfur compounds. Closures must seal tightly to prevent leakage, and lubricants, when necessary, selected with care to prevent loss of the sample or its contamination. Packless valves are frequently used with metal containers.

**Sample Lines**—With regard to materials for sample lines the same rules must apply as for sample containers. They must not permit loss of sample constituents or contaminate the sample in any way. Rubber tubing is permeable to hydrogen and light hydrocarbons and swells and deteriorates in contact with either aliphatic or aromatic hydrocarbons. Sulfur used in vulcanizing rubber can contaminate

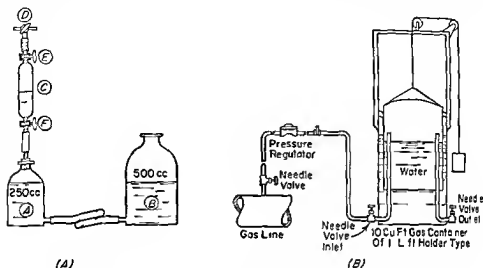


FIG 35-2 Sample Collecting Apparatus Atmospheric Pressure (Reproduced with permission from ASTM Standards ASTM Philadelphia 1958)

samples and is detrimental when traces of sulfur compounds in the gas are to be determined. Plastic tubing such as Tygon or polyethylene has been successfully used in many cases. Aluminum tubing is frequently used when acidic gases are absent. Iron brass and steel pipe are useful.

The size of the sample tube in diameter and length should be limited to that required for ease of handling. Before a sample is collected it must be purged of any gases present in it so that it is evacuated completely or filled with a portion of the gas to be collected. When large sample lines are to be installed permanently for continuous or periodic collection of samples from given equipment or processes it is good practice to purge the line continuously at a rate such that the residence time of a volume of gas in the line is very small.

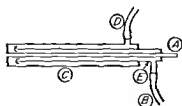


FIG 35-3 Water Cooled Sampling Probe (Reproduced with permission from ASTM Standards ASTM Philadelphia 1958)

If conditions are such that some constituent of the gas is likely to condense in the line during collection of the sample it is frequently necessary to heat it by a companion steam line, electrical heating tapes or jackets.

For withdrawing samples of combustion products from furnaces or boilers a metal water cooled sample probe is recommended (Fig 35-3). The water jacket not only protects the sample tube and prevents its destruction but also chills the sample rapidly to minimize changes in composition which may take place in the process of sampling.



**Containing Fluids.**—Many gas samples are taken, especially those at atmospheric pressure, by displacing a confining liquid initially filling a sample container. Precautions must be observed with this practice to prevent loss of constituents by solution in the confining liquid or contamination of the sample by the release of gases which had dissolved in it.

Mercury is a nearly ideal liquid for this purpose. It will, however, react chemically with gas samples containing hydrogen sulfide, mercaptans, and some other sulfur-bearing compounds. It cannot be used with brass or copper containers, nor with any container having soldered joints. It is often, however, not easy to handle because of its weight, and in addition its cost can limit the desirability of using large quantities.

Water is a more common confining liquid. Many gases, however, will dissolve in it to a greater or lesser extent, as illustrated by a few common examples in Table 35-1. Losses of constituents can be minimized by saturating the water, prior

TABLE 35-1. SOLUBILITY OF SOME COMMON GASES IN WATER

Gas	Solubility
Nitrogen	0.0140
Oxygen	0.0277
Hydrogen	0.0172
Carbon monoxide	0.0209
Carbon dioxide	0.739
Hydrogen sulfide	2.225
Methane	0.0294
Ethane	0.0415
Ethylene	0.1064
Acetylene	0.811

Solubility is expressed as number of ml. of gas, measured at 25°C., 760 mm., dissolved in 1 ml. of water at equilibrium at 25°C. and a total pressure (gas and water vapor) of 760 mm. Solubilities calculated from Henry's constants given in International Critical Tables, Vol. III, McGraw-Hill, N. Y., 1928.

to its use for collecting a sample, with the gas to be sampled. Equilibration can be facilitated by bubbling the gas through the water. Reduction of such losses can be further aided by using nearly saturated solutions of sodium chloride or magnesium chloride slightly acidified with hydrochloric acid.

The need for confining fluids can sometimes be avoided by using containers initially evacuated, or by purging a dry container by passing the gas to be sampled through it for sufficient time. Adequate purging should be attained with a volume of gas not less than ten times the volume of the container.

**Metering Samples.**—In many procedures requiring continuous sampling and analysis, and especially the use of automatic analytical instruments, the rate at which the sample is supplied, as well as its total volume, is metered. This frequently occurs with analysis of process gas streams in the petroleum and fuel gas industries, or of flue, boiler, and furnace gases.

Because of possible losses of soluble constituents, especially in those cases where trace quantities are to be determined, the location of the wet-test meters between sample source and analytical apparatus is to be avoided; calibrated capillary or

orifice flowmeters and rotameters are superior in this respect. Their volumetric accuracy within  $\pm 1\%$  with careful calibration is usually sufficient. Dry positive displacement meters may sometimes be used if the sample size falls within their range of utility.

Standard methods to be used in the measurement of gaseous fuel samples are described in ASTM Designation D1071-55.<sup>4</sup> They are applicable to the measurement of gaseous fuel samples including liquefied petroleum gases in the gaseous state at normal temperatures and pressures. The variety of equipment included is listed in Table 35-2. Conditions accompanying the calibration and use of the different forms of measuring apparatus are included in the methods given.

TABLE 35-2 APPARATUS FOR MEASURING GASEOUS FUEL SAMPLES  
(ASTM D1071-55)

#### Containers

- Cubic foot bottle—immersion type or moving tank type
- Portable cubic foot standard (Sullman type)
- Fractional cubic foot bottle
- Burets, flasks, etc. for chemical and physical analysis
- Calibrated gasometers (gas meter provers)

#### Gas meters—displacement type

- Liquid sealed rotating drum meters
- Diaphragm or bellows type meters equipped with observation index
- Rotary displacement meters

#### Gas meters—rate of flow type

- Porous plug and capillary flowmeters
- Float (variable area—constant head) flowmeters
- Orifice flow nozzle and venturi type flowmeters

**Collection Procedures**—The analyst is referred to ASTM Standard Methods for a detailed description of specified methods for sampling manufactured natural or liquefied petroleum gases. The following digest of the salient requirements, in addition to those previously described, will be useful in those situations of general practice not necessarily requiring strict compliance with specifications.

Procedures for taking samples at atmospheric pressure follow the principles previously outlined, with precautions against the loss of carbon dioxide, hydrogen sulfide, and the other constituents soluble in the usual aqueous conditioning fluids. Sampling natural gas under pressure requires due caution in handling pressures which may be as high as 1200 psi in transmission lines or up to 10,000 psi as in some gas wells. Illustrations of apparatus for collecting gas samples under pressure are found in Fig. 35-1(A).

In liquefied petroleum gases the major components are propane and butane. If one of these predominates, the other plus smaller quantities of higher or lower hydrocarbons usually accompanies it. The source may be natural gas, oil scrubbed from natural gas, or by-product gases of the petroleum refining and processing industry. The latter may contain small amounts of unsaturated hydrocarbons such as propylene or butylenes.

<sup>4</sup> Standard Method for Measurement of Gaseous Fuel Samples, D1071-55, ASTM Standard and Part 8, American Society for Testing and Materials, Philadelphia, Pa., p. 1193, 1955.

If the sample for analysis is taken from a quantity existing already in the gaseous state, at atmospheric pressure for example, and remains a gas in its container until analyzed, the sampling principles already described will apply. However, liquefied petroleum gases, as the name implies, are readily condensed to liquid under pressure, and are most often available in this state, so that liquid samples must be collected. The vapors above such a liquid mixture do not have the same composition as that of the liquid. Moreover, a gaseous sample taken from a nearly full container of liquefied petroleum gas will differ from one taken after it is nearly emptied.

Metal sample containers designed to withstand pressure, and to contain liquid samples, as recommended by ASTM, are illustrated in Fig. 35-1(B).

The ASTM Standard Method for Sampling Liquefied Petroleum Gases (D1265-55) further states that considerable effort may be required to obtain a representative sample, especially if the material being sampled is a mixture of liquefied petroleum gases. The following factors must be considered:

Obtain samples of the liquid phase only.

When it is definitely known that the material being sampled is composed predominantly of only one liquefied petroleum gas, a liquid sample may be taken from any part of the vessel.

When the material being sampled has been agitated until uniformity is assured, a liquid sample may be taken from any part of the vessel.

Because of wide variation in the construction details of containers for liquefied petroleum gases, it is difficult to specify a uniform method for obtaining representative samples of heterogeneous mixtures.

Directions for sampling cannot be made explicit enough to cover all cases. They must be supplemented by judgment, skill, and sampling experience. Extreme care and good judgment are necessary to insure samples which represent the general character and average condition of the material.

Keep samples in a cool location until all tests have been completed. Discard any samples in containers which develop leaks. Protect the valves on the sample container, either by packing the container in a crate in an approved manner or by using a protective cap, so that accidental unseating of the valve or tampering with it is avoided.

## DETERMINATION OF MAJOR CONSTITUENTS

The major constituents of a fuel gas are often considered those that are present in a mixture in concentrations greater than some small value, say 0.5% by volume. These have in the past been determined by basic chemical absorption methods of analysis, and were necessarily then limited to carbon dioxide, oxygen, unsaturated hydrocarbons (as a group), carbon monoxide, hydrogen, nitrogen, methane, and ethane. With the development of more sensitive and sophisticated methods of analysis in recent years, individual hydrocarbon species are routinely determined. Selection of an analytical method depends on the chemical nature of the mixture to be analyzed, the purpose for which the information is desired, and to a large extent on the value of the data in relation to the substantial cost of modern analytical instruments.

## CONSTANT PRESSURE VOLUMETRIC ANALYSIS

The techniques and apparatus for chemical absorption analysis remain a basic procedure for a great many routine industrial gas analyses. The method is simple in concept, and the apparatus is inexpensive and easily manipulated. Much valuable information about gas composition, manufacturing, and utilization processes can be gained by its use. Modern analytical instruments such as the mass spectrometer, chromatographic and low temperature fractionation equipment, produce much more detailed analyses sometimes in a shorter time, and with less effort on the part of the operator. However, this is achieved only with a considerable investment in the apparatus, and with greater maintenance demands because of its complexity.

In constant pressure volumetric analysis the sample of gas is first subjected successively to a series of chemical reagents, each of which removes a single constituent from the sample. The decrease in volume of the sample, during treatment with each reagent, represents the volume of constituent removed in that step, all volume measurements being made at a constant (approximately atmospheric) pressure. Hydrogen, carbon monoxide, and lower paraffin hydrocarbons in fuel gases are determined by combustion procedures with equipment incorporated in the analytical apparatus. The composition of the original sample is then expressed in volume per cent of each constituent present.

## ABSORBENT REAGENTS

Typical absorbent reagents to be used in the successive steps of the absorption analysis, as adapted from Altner,<sup>5</sup> are described below. The concentrations suggested represent good practice and will give reliable results, although they need not be rigidly adhered to. Concentrations for solutions found in ASTM Standard Method D1136 53<sup>6</sup> are slightly different, but this only indicates the flexibility of composition found in many references.

**Absorbents for Carbon Dioxide.**—Carbon dioxide is rapidly absorbed in a strong solution of either sodium or potassium hydroxide. Sodium hydroxide has a greater chemical action on glass and more quickly forms a bicarbonate precipitate which tends to clog the capillaries of the pipets, potassium hydroxide solution is therefore preferable. If the gas mixture contains hydrogen sulfide, sulfur dioxide and other acid gases, they will be absorbed in the caustic solution and determined as carbon dioxide.

**Potassium Hydroxide.**—Dissolve 300 g. of A.C.S. grade potassium hydroxide sticks or pellets in 1000 ml. of distilled water. Add the hydroxide slowly and stir until completely dissolved. Do not shake in a stoppered flask or bottle to effect solution, and avoid contact with skin or clothing. Preserve the solution in a rubber stoppered bottle and allow any solid material to settle before using. (Sodium hydroxide is prepared by dissolving 200 g. of sodium hydroxide in 1000 ml. of distilled water, as with potassium hydroxide.)

**Absorbents for Unsaturated Hydrocarbons.**—Unsaturated hydrocarbons, or that group sometimes termed "illuminants," are usually absorbed by fuming sulfuric

<sup>5</sup> Altner, V. J., *Gas Analysis and Testing of Gaseous Materials*, American Gas Association N. Y., 1945.

<sup>6</sup> Standard Method for Analysis of Natural Gases by the Volumetric Chemical Method D1136 53 ASTM Standards, Part 8, American Society for Testing and Materials Philadelphia, Pa., p. 1218, 1958.

acid or bromine water. In manufactured or coke oven gases, the "illuminants" fraction contains ethylene, propylene, butylene, benzene, toluene, and acetylene, with perhaps ethylene and benzene predominating. All of these are removed by fuming sulfuric acid. Long contact with this reagent will cause a significant absorption of the higher paraffins, if present, especially if the fuming sulfuric acid is fresh and the partial pressure of the higher paraffins is high. Bromine water absorbs ethylene and its homologues satisfactorily, but it is not entirely satisfactory for absorbing benzene. Since the reagents are volatile, the gas sample must be treated with caustic solution to remove the sulfur trioxide or bromine fumes before measuring the residual volume.

**Fuming Sulfuric Acid.**—Sulfuric acid containing, when fresh, 15% free  $\text{SO}_3$  is recommended.

**Bromine Water.**—Add bromine to water until an excess of liquid bromine remains in the bottom of the bottle or pipet. A small amount of potassium bromide (about 5% by weight) may be added to the water in order to make the bromine more soluble. Care should be taken to avoid contact of bromine with the skin or clothing.

**Absorbents for Oxygen.**—Alkaline pyrogallol is most frequently used for absorption of oxygen, although chromous chloride is sometimes recommended.

**Alkaline Pyrogallol.**—Add to each 100 ml. of KOH solution described above, 17 g. of reagent grade pyrogallol crystals. Protect the resulting solution from air in a glass-stoppered reagent bottle, and place in a refrigerator to keep cool until the crystals are dissolved. This solution will generate no significant amount of CO in use.

**Chromous Chloride.**<sup>5</sup>—Stable solutions are best made by reducing the salt in a Jones, or amalgamated zinc, reductor. To prepare the reductor, 5 g. of mercury are dissolved in dilute nitric acid (1:1), the solution diluted to 250 ml., and transferred to a 1-liter flask. About 500 g. of 20-mesh granular zinc are put into the flask and shaken for several minutes. After standing for 10 to 15 min., the zinc is washed with water by decantation. A layer of glass beads is placed in the reductor tube, the beads covered with glass wool, and a thin layer of asbestos is spread upon the glass wool. The amalgam, which is always kept covered with water, is poured in upon the asbestos mat, washed once with a 5% solution of sulfuric acid, and then with water until free from acid. A solution of 75 g. of chromic chloride in 190 ml. of water, acidified with 10 ml. of hydrochloric acid, is added to the reductor until the water at the bottom of the reductor becomes colored. The bottom of the reductor is attached, by means of a rubber stopper carrying a small Bunsen valve, to the rear chamber of a pipet filled with a gas free from oxygen, and the remainder of the solution is allowed to flow drop by drop through the reductor into the pipet until sufficient has collected to fill it to the proper level. The pipet is immediately connected to the apparatus, and the solution kept carefully protected from the air. This solution will give off no hydrogen and will absorb all the oxygen in from two to four passes through a bubbling pipet.

**Absorbents for Carbon Monoxide.**—Carbon monoxide is usually absorbed by either acid cuprous chloride solution, or cuprous sulfate-beta-naphthol solution. For satisfactory results it is necessary to use two pipets, one to absorb most of the carbon monoxide and the other to take out the last significant traces. When two pipets are used in series, the filling and order of use may be alternated; that is, the last one filled becomes the one used for removing the last traces.

**Acid Cuprous Chloride**<sup>7</sup>—Dissolve 450 g of c p cuprous chloride in 2000 ml of c p hydrochloric acid sp gr 1.18. Some laboratories use a weaker solution composed of 75 g of cuprous chloride in 600 ml of concentrated hydrochloric acid and then diluted with water to make 1000 ml. The latter preparation gives off less hydrochloric acid vapor than the more concentrated acid solution. Oxygen is rapidly absorbed by acid cuprous chloride solution and the cuprous chloride is oxidized to an appreciable extent during the preparation. The solution may be a greenish black color immediately after preparation or on standing and must be reduced until it assumes a clear straw yellow color. Add strips of sheet copper, copper turnings, wire or gauze to the storage bottle. The solution is ready for use when it becomes a light straw color.

**Cuprous Sulfate Beta Naphthol Solution**—This absorbs carbon monoxide quantitatively but not as rapidly as fresh acid cuprous chloride. With samples containing small amounts of carbon monoxide as flue gas it is a very satisfactory reagent but for samples containing large amounts of carbon monoxide two pipets in series are recommended: one containing acid cuprous chloride for absorbing the major portion of the carbon monoxide and the other cuprous sulfate beta naphthol for absorbing the final traces. In the latter solution cuprous sulfate reacts with carbon monoxide to form  $\text{Cu}_2\text{SO}_4 \cdot 2\text{CO}$ . This is a stable compound and the solution does not give up carbon monoxide as does cuprous chloride. While the mixture will absorb about 18 ml of carbon monoxide per ml of solution the action is very slow after it has become half saturated although it is complete if sufficient contact is given. The reagent also absorbs ethylene and its homologues and a little oxygen but does not absorb methane and other saturated hydrocarbons, hydrogen and nitrogen. It is most satisfactorily obtained already made from supply houses sometimes under proprietary names such as Cosorbent.<sup>7</sup>

### APPARATUS AND PROCEDURE

Modern equipment for volumetric gas analysis has been developed from the Orsat apparatus in which a series of pipets is semipermanently connected with a measuring buret through a capillary manifold. Most laboratory and technical supply houses introduce their own variations of construction and complement of pipets. Their operation or manipulation however usually conforms with the same fixed pattern. In portable forms the confining fluid is usually water; the number of pipets is frequently limited to three or four; combustion steps are usually though not always omitted; pressure and temperature compensators are not used. Laboratory forms are more versatile and are required for complete fuel gas analysis. Mercury rather than water is used as the confining fluid. Combustible constituents other than carbon monoxide can be determined and sometimes special reagents applicable to particular or unusual needs are employed.

### ANALYSIS WITH PORTABLE ORSAT APPARATUS

The portable Orsat apparatus enclosed in a wooden carrying case is adapted for flue gas or furnace gas analysis. It uses a shortened buret as it is unlikely that the sum of carbon dioxide, oxygen and carbon monoxide in the sample will

<sup>7</sup> Cosorbent is a registered trade mark for this reagent as supplied by Burrell Corporation, 2223 Fifth Avenue, Pittsburgh 19, Pa.

exceed 50 ml. The pipets are filled, in order starting from that nearest the buret, with alkali, pyrogallol, and cuprous chloride solutions.

After filling the pipets with the appropriate solutions, and before making an analysis, bring all solution levels to the engraved index marks on the pipet capillary tubes by withdrawing the air from above the solutions, successively into the buret, by lowering the leveling bottle.

Open the buret stopcock to the atmosphere, and raise the leveling bottle until the buret is filled with water. After connecting the sample bottle to the inlet capillary tube, draw a portion of the gas sample into the buret. Close the buret stopcock. By holding the leveling bottle near the buret, adjust the water levels to the same height (atmospheric pressure) and read the volume of gas in the buret.

Open the buret stopcock to the manifold, and the stopcock of the alkali pipet. By raising and lowering the leveling bottle, pass the gas into the pipet from the buret and back again. Carbon dioxide should be removed from the sample in from three to five passes into the alkali solution. Return the residual sample to the buret, carefully drawing the solution in the pipet exactly to the engraved index mark on the capillary neck. Close the pipet stopcock. Again adjust the water levels in the buret and leveling bottle and read the remaining volume of gas. Make additional passes into the KOH until there is no further reduction in volume. If the initial volume of sample taken into the buret is  $V_1$ , and the volume after removing  $\text{CO}_2$  is  $V_2$ , then

$$\text{per cent CO}_2 = 100 \frac{V_1 - V_2}{V_1}.$$

By skillful manipulation the initial volume,  $V_1$ , can easily be made exactly 100 ml., thereby simplifying the calculations.

In a similar manner, oxygen in the sample is removed by successive passes through the pyrogallol solution in the second pipet. Measurement of the residual volume,  $V_3$ , after its complete removal gives

$$\text{per cent O}_2 = 100 \frac{V_2 - V_3}{V_1}.$$

Remove carbon monoxide by successive passes through the cuprous chloride solution. After each series of passes (say five or more), and before measuring the residual volume, pass the gas into the KOH pipet to remove hydrochloric acid vapors evolved from the acid cuprous chloride. Then the volume after removing CO is  $V_4$ , and

$$\text{per cent CO} = 100 \frac{V_3 - V_4}{V_1}.$$

The gas analysis is usually completed with this step, although hydrogen, traces of hydrocarbons, and sometimes the CO as well may be determined by combustion procedures similar to those described in the following sections.

#### COMPLETE ANALYSIS WITH LABORATORY APPARATUS

Gas analysis equipment located more or less permanently in a laboratory is adapted to more general, and more precise analyses. Figure 35-4 illustrates laboratory apparatus of this kind. In this equipment precision is increased by using

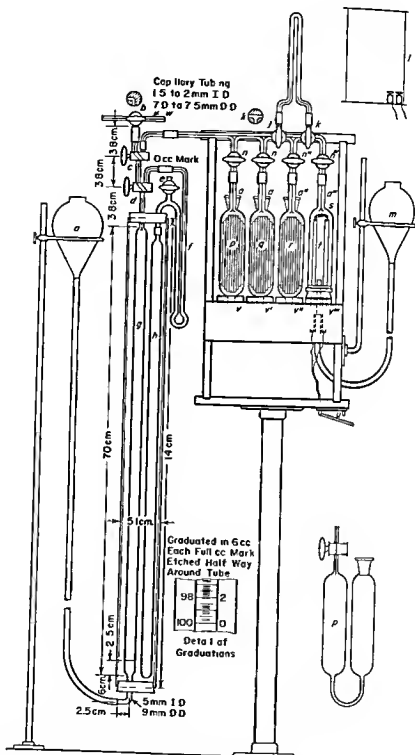


FIG 35-4 U S Steel Type Gas Analysis Apparatus Front View a Leveling B lb b, 3 way L Bore Cock c and d 3 way Parallel Bore Cocks e 2 way Cock f Mercury or Oil Mark, g, Buret, h, Pettersson Compensating Tube i Copper Oxide Tube j and k

FIG 35-4 (Continued on page 1519)



mercury as a confining fluid, and by providing compensation for possible changes in ambient laboratory temperature and barometric pressure during an analysis.

**Apparatus.**—Although apparatus from different manufacturers differ in details, they all consist of a series of pipets connected through a capillary tube manifold to a buret. The buret is enclosed in a water jacket and provided with a device to compensate for changes in temperature and barometric pressure which may occur during the period of an analysis. A slow-combustion pipet, with leveling bulb, filled with mercury is included, and in most forms there is a fractional combustion tube containing copper oxide. The latter is equipped with a heater to maintain its temperature at the desired level. In many models provision is made for several supplementary pipets to contain additional or special absorption reagents.

Analytical procedures also differ in details, depending on the nature of the gas to be analyzed. Natural gases, containing no hydrogen or carbon monoxide, may be analyzed according to ASTM Standard Method D1136-53,<sup>8</sup> from which the following is adapted. Six pipets are called for, arranged in the following sequence:

1. Simple bubbling or contact pipet containing KOH.
2. Simple bubbling pipet containing fuming sulfuric acid.
3. Distributing-tip bubbling pipet<sup>9</sup> containing alkaline pyrogallol.
4. Slow combustion pipet with platinum wire spiral.
5. Duplicate of (1).
6. Duplicate of (3).

**Preparation of Apparatus.**—Test the assembled apparatus for leaks by applying approximately 15 cm. (6 in.) mercury gage positive, then negative pressure, and measuring any change in volume that may occur as one after another the sections of the apparatus are opened to the buret at 5- or 10-minute intervals.

Equilibrate the reagents with respect to the sample to be analyzed. For usual work, equilibrate by making six passes into each reagent, using the gas that is to go into each reagent during the actual analysis.

Wet the buret wall with a film of water by taking several milliliters of water into the buret and slowly expelling it.

Flush the manifold, pipet inlets, and arm of manometer connected to the manifold with nitrogen, and balance to the reference (compensator) pressure.

**Absorption Analysis.**—Transfer about 95 to 100 ml. of the sample to the buret without contamination, allow 3 minutes to saturate the sample with respect to water if it is dry, and then adjust the pressure until the manometer indicates the

<sup>8</sup> Standard Method of Analysis of Natural Gases by the Volumetric-Chemical Method. D1136-53. A.S.T.M. Standards. Part 8, American Society for Testing and Materials, Philadelphia, Pa., p. 1218, 1958.

<sup>9</sup> Shepherd, M., N.B.S. Journal of Research, 6, 121, 1931, R.P. 266.

FIG. 35-4. (Continued from page 1518)

Stopcocks: *l*, Electric Furnace for Copper Oxide Tube; *m*, Mercury Bath; *n*, *n'*, *n''*, and *n'''*, Cocks; *o*, *o'*, and *o''*, Reagent Marks; *o'''*, Mercury Mark; *p*, Pipet to Remove CO<sub>2</sub>; *q*, Pipet to Remove Illuminants; *r*, Pipet to Remove O<sub>2</sub>; *s*, Ends of Platinum Coil; *t*, Pipet to Determine CH<sub>4</sub> and C<sub>2</sub>H<sub>6</sub>; *u*, Switch; *v*, *v'*, *v''*, and *v'''*, Supports for Pipets. (Reproduced with permission from A. C. Fieldner, G. W. Jones, and W. F. Holbrook. The Bureau of Mines Orsat Apparatus for Gas Analysis. U. S. Bureau of Mines Technical Paper, 320.)

sample is at the reference (compensator) pressure. Measure this volume  $V_1$  to the nearest 0.02 ml.

**Carbon Dioxide or Acid Gases**—Displace the gas in the arm of the manometer connected to the distributor (manifold) into the buret and then transfer the sample to the KOH pipet 1. Return the gas to the buret and pass twice more into the KOH solution then allow to stand 3 minutes in the buret, balance the manometer and measure the volume  $V_2$  to the nearest 0.02 ml.

**Unsaturated Hydrocarbons**—Displace the gas from the manometer arm and pass twice in and out of pipet 2, once into pipet 1 then once again into pipet 2 and twice into pipet 1. Finally measure the volume of  $V_3$  of the gas after letting it stand 3 minutes in the buret.

**Oxygen**—Displace the gas from the manometer arm and pass twice into pipet 3, once each into pipets 1 and 2 and finally twice more into pipet 3. Measure the residual volume  $V_4$ .

This completes the absorption steps. With natural gas the succeeding combustion steps are performed with a second portion of the sample. For manufactured gas proceed to the fractional combustion of hydrogen and carbon monoxide described later.

**Combustion Analysis**—Prepare nitrogen for use as a transfer gas by absorption of oxygen from uncontaminated air in pipet 6. Flush the distributor with this nitrogen and balance to reference pressure then measure about 40 ml of the nitrogen  $V_5$  and transfer it for storage over the KOH solution in pipet 3. (Pipets 3 and 6 are supplemental pipets.)

Measure about 95 ml of approximately pure and carefully analyzed oxygen  $V_6$  and transfer to the slow combustion pipet. Let  $V$  represent the volume of the inert impurities in this oxygen.

Measure a fresh sample  $V_8$  of gas for combustion analysis (about 35 ml or less than 35 ml when the proportion of heavier hydrocarbons is great). If the absorption analysis shows more than 0.2% unsaturated hydrocarbons pass this sample through fuming sulfuric acid before the combustion analysis. Adjust the pressure in the buret and slow combustion pipet to atmospheric with the platinum wire glowing dull red then open the combustion pipet to the buret and slowly pass the sample over the hot platinum spiral. Allow fully 15 minutes for the first passage of sample into the combustion zone. When the sample has all left the buret, displace the gas from the manometer arm connected to the distributor and pass this into the combustion pipet. Then return the gas from the combustion pipet to the buret until the mercury is just under the platinum spiral, take about 5 minutes for this and reverse the flow to return the gas to the combustion pipet. Three more complete passes to and from the buret should complete the combustion. On the last pass allow the gas in the combustion pipet to cool before returning to the buret. Measure the residue  $V_9$ .

**Removal of  $\text{CO}_2$  Produced**—Displace the gas from the manometer and pass three times from the buret into the KOH solution in pipet 5, once into the combustion pipet and once more into pipet 5. Measure the residue  $V_{10}$ .

**Removal of Excess Oxygen**—Displace the gas from the manometer and pass four times into pipet 6, once into pipet 5, once into the combustion pipet and once again into pipet 6. Measure the residue,  $V_{11}$ .

**Calculations**—From the results of the absorption analysis calculate the percentages of carbon dioxide, unsaturated hydrocarbons and oxygen present in the original sample, as follows:

$$\text{carbon dioxide (or acid gas), per cent} = \frac{V_1 - V_2}{V_1} \times 100,$$

$$\text{unsaturated hydrocarbons, per cent} = \frac{V_2 - V_3}{V_1},$$

$$\text{oxygen, per cent} = \frac{V_3 - V_4}{V_1} \times 100,$$

where  $V_1$  = volume of sample taken for absorption analysis,

$V_2$  = volume of sample after removal of  $\text{CO}_2$  (acid gases),

$V_3$  = volume of sample after removal of unsaturated hydrocarbons, and

$V_4$  = volume of residual gas after removal of oxygen.

Calculate the results of the combustion analysis as follows:

$$\text{TC} = V_6 + V_8 - V_9,$$

$$V_{12} = (V_1 - V_2) \frac{V_8}{V_1},$$

$$V_{13} = (V_3 - V_4) \frac{V_8}{V_1},$$

$$\text{CO}_2 = V_5 + V_9 - V_{10} - V_{12},$$

$$\text{O}_2 = V_6 - V_7 + V_{13} - (V_{10} - V_{11}),$$

$$\text{N}_2 = V_{11} - V_5 - V_7,$$

$$\text{CH}_4, \text{ per cent} = \frac{1}{3}[7(\text{TC} + \text{CO}_2) - 9\text{O}_2] \frac{100}{V_8}, \text{ and}$$

$$\text{C}_2\text{H}_6, \text{ per cent} = \frac{1}{3}[6\text{O}_2 - 4(\text{TC} + \text{CO}_2)] \frac{100}{V_8},$$

where TC = total contraction of sample upon combustion,

$\text{CO}_2$  = carbon dioxide produced by combustion of the sample,

$\text{O}_2$  = oxygen consumed,

$V_1$  and  $V_2$  = values defined under Absorption Analysis,

$V_5$  = volume of nitrogen taken as a transfer gas,

$V_6$  = volume of oxygen taken for combustion (the actual volume of pure oxygen being  $V_6$  corrected),

$V_7$  = volume of inert impurities in the oxygen taken for combustion,

$V_8$  = volume of sample taken for combustion,

$V_9$  = volume of residual gas after combustion of sample,

$V_{10}$  = volume of residue after removal of  $\text{CO}_2$  produced by combustion, plus the transfer nitrogen,

$V_{11}$  = volume of residue after removal of excess  $\text{O}_2$ , plus the transfer nitrogen,

$V_{12}$  = volume of  $\text{CO}_2$  originally present in the sample, and

$V_{13}$  = volume of  $\text{O}_2$  originally present in the sample.

In the analysis of manufactured gases containing substantial proportions of hydrogen and carbon monoxide and correspondingly smaller amounts of hydrocarbons, fractional combustion over hot copper oxide may be used. Absorption anal-

ysis is performed in accordance with the preceding procedure, and the residual volume  $V_4$  remains after absorption of oxygen

**Fractional Combustion**<sup>10 11 12</sup>—The temperature of the fractional combustion tube, which has been flushed with nitrogen, is adjusted to 290 to 310°C

Pass the sample slowly through the heated copper oxide tube by transfer from the buret to the slow combustion pipet and return. During the transfer maintain substantially atmospheric pressure by judicious adjustment of the mercury levels in the buret and pipet. After returning the sample to the buret measure its volume, adjusting to reference (compensator) pressure. Contraction occurs when  $H_2$  is converted to water, and  $CO_2$  is formed from the  $CO$  present. Pass the sample into the  $KOH$  pipet to absorb the  $CO_2$ . Measure the residual volume. Pass the sample again through the copper oxide, measure the contraction and the  $CO$  formed as indicated by absorption in  $KOH$ . Repeat until contraction and  $CO$  formation are each less than 0.05 ml. Record remaining volume,  $V_{12}$ .

If  $V_{10}$  is the sum of the measured contractions after each pass, and  $V_{11}$  is the total  $CO_2$  formed by combustion, then

$$\text{per cent } H_2 = 100 \left( \frac{V_{10}}{V_1} \right)$$

$$\text{per cent } CO = 100 \left( \frac{V_{11}}{V_1} \right)$$

The residual volume,  $V_{12}$ , containing only hydrocarbons and nitrogen is then burned by slow combustion with oxygen over the heated platinum wire as described in the preceding procedure. Calculate hydrocarbons as methane and ethane after the slow combustion as follows

$$\text{volume of } C_2H_6 = \frac{2}{3}(2CO_2 - \text{contraction})$$

$$\text{volume of } CH_4 = CO_2 - 2C_2H_6$$

Multiplying the volumes of hydrocarbons found by the ratio representing the portion of  $V_{12}$  taken for combustion to obtain per cent by volume of each constituent in the original sample we can make the following calculations

$$\text{per cent } C_2H_6 = 100 \frac{V_{12} \text{ Volume of } C_2H_6}{V_{13} V_1}$$

$$\text{per cent } CH_4 = 100 \frac{V_{12} \text{ Volume of } CH_4}{V_{13} V_1}$$

where  $V_{13}$  is that portion of  $V_{12}$  actually burned

The nitrogen content of the original sample may be determined by difference if the excess oxygen taken for combustion is not absorbed

$$\text{per cent } N_2 = 100 - (\% CO_2 + \% O_2 + \% \text{ "Illuminants"}$$

$$+ H_2 + \% CO + \% \text{ paraffin hydrocarbons})$$

<sup>10</sup> Altieri, V. J., *Gas Analysis and Testing of Gaseous Materials*. American Gas Association, N. Y., 1945

<sup>11</sup> Fieldner, A. C., Jones, G. W., and Holbrook, W. F. Technical Paper No. 320 U. S. Bureau of Mines, 1925

<sup>12</sup> Methods of the Chemists of the U. S. Steel Corporation for the Sampling and Analysis of Gases. Carnegie Steel Company, Pittsburgh, Pa., 1927

## CORRECTIONS FOR DEVIATION FROM IDEAL GAS LAW

In the preceding calculations it is assumed that all component gases involved behave like an ideal gas, with a molecular volume of 22.412 l. at 0°C. and 760 mm. Hg pressure. For ordinary fuel gas analyses this assumption is sufficiently valid. However, more precise results may be desired, necessitating corrections for deviations from ideal gas behavior.

According to Altieri, significant deviations can occur only when carbon dioxide, methane, ethane, and the higher paraffin hydrocarbons found in natural gas are present. He states that "... in order to avoid the use of corrected equations in calculating percentages from combustion data the quantity of sample taken should be such that the carbon dioxide does not exceed 30 per cent of the total gas measured after combustion. This rule is applicable to most manufactured fuel gases, since the respective partial pressures of the constituents determined by combustion are usually sufficiently low to permit keeping the carbon dioxide below 30 per cent partial pressure, and yet employ enough sample to avoid large manipulation errors. Burrell<sup>13</sup> however, states that for the precise analysis of mixtures in which the carbon gases constitute almost the whole of the sample (as natural gas) it is better to use the slow-combustion method, thereby using a large volume of sample, and apply corrections for deviation from gas laws. Also, when necessary, these corrections should be used in slow-combustion analysis of prepared combustible gases that are being examined for purity."<sup>14</sup>

TABLE 35-3. RELATIVE MOLECULAR VOLUMES (PERFECT GAS = 1)

<i>Pressure</i> <i>mm. Hg</i>	<i>Relative Molecular Volume</i>	
	<i>CO<sub>2</sub></i>	<i>C<sub>2</sub>H<sub>6</sub></i>
100	0.999	0.999
200	0.999	0.997
300	0.998	0.996
400	0.997	0.995
500	0.997	0.994
600	0.996	0.992
700	0.995	0.991
760	0.995	0.990

For reference, Table 35-3 gives useful data on the deviation from ideal behavior of carbon dioxide and ethane. It seems likely that these are the only two constituents likely to require the use of the deviation corrections. Burrell and Seibert<sup>13</sup> may be referred to if more detailed procedure is desired.

## REPRODUCIBILITY OF VOLUMETRIC ANALYSES

Shepherd,<sup>15</sup> in cooperation with the American Society for Testing and Materials and about fifty analytical laboratories, made extensive studies of the precision of this type of gas analysis. Gas mixtures were synthesized, by mixing individual

<sup>13</sup> Burrell, G. A., and Seibert, F. M., Technical Paper No. 54, U. S. Bureau of Mines, 1913.

<sup>14</sup> Altieri, V. J., Gas Analysis and Testing of Gaseous Materials, American Gas Association, N. Y., p. 146, ref. 1, 1945.

<sup>15</sup> Shepherd, M., N.B.S. Journal of Research, **36**, 313, 1946, R.P. 1704; **38**, 19, 1947, R.P. 1759.

components, to represent two types of fuel gas frequently analyzed. One had a composition similar to that of a carburetted water gas, the other was composed of hydrocarbons and simulated a natural gas. Examination of the data from many analyses of these two samples permits an estimate to be made of the accuracy and reproducibility of determination of some components. The following conclusions (from ASTM Standard Method D1136 53) refer specifically to the components in natural gas but should be applicable to the manufactured gas as well.

Since it is not possible to determine more than two saturated hydrocarbons by this method and the errors caused by the presence of other hydrocarbons depend upon their identity and amounts, no statement can be made concerning the actual accuracy of the method with respect to the hydrocarbons. Any  $C_3H_8$  would be calculated as  $2C_2H_6-CH_4$ ,  $C_3H_{10}$  would be calculated as  $3C_2H_6-2CH_4$  and so on.<sup>16</sup>

The accuracy of determination of other components and the precision of all are shown in the following table.

Gas	Probable Accuracy	Reproducibility	
		Different Laboratories and Apparatus	One Laboratory and Apparatus
Carbon dioxide, per cent	0.05	0.04	0.02
Oxygen, per cent	0.1 to 0.2	0.1	0.03
Unsaturated hydrocarbons as a group, per cent			0.01
Nitrogen, per cent	0.6	0.6	0.1
Methane, per cent		1.0	0.2
Ethane, per cent		1.0	0.2

For the carburetted water gas sample,<sup>15</sup> concentrations of  $H_2$ , CO, and unsaturated (as a group) found by analysis appear to have a precision approximately the same order as values indicated for other components.

### LOW TEMPERATURE FRACTIONAL DISTILLATION ANALYSIS

The analysis of light hydrocarbon gases by low temperature distillation procedures may be performed with a high degree of reliability and precision when modern apparatus and techniques are employed. The method involves the separation and identification of the constituents of a mixture according to their boiling points, and quantitative measurement of their concentration by the pressure built up by each fraction collected in evacuated and calibrated reservoirs. The method finds its principal use in the analysis of natural gases, liquefied petroleum gas, petroleum refinery and chemical manufacturing process streams.

Summaries of early work and related procedures are to be found in Altieri<sup>17</sup> and Denny and Luxon.<sup>18</sup> The development of distillation procedures appears to

<sup>16</sup> Standard Method of Analysis of Natural Gases by the Volumetric Chemical Method D1136 53. ASTM Standards, Part 8. American Society for Testing and Materials, Philadelphia, Pa., p. 1218, 1958.

<sup>17</sup> Altieri, V. J., Gas Analysis and Testing of Gaseous Materials, Chap. XV, American Gas Association, N. Y., 1915.

<sup>18</sup> Denny, L. C., and Luxon, L. L. (ed.) Handbook of Butane-Propane Gases, 3rd ed., Jenkins Publications, Los Angeles, 1951.

TABLE 35-4. BOILING POINTS OF FUEL GAS COMPONENTS  
(At atmospheric pressure)

	<i>Boiling point</i>	
	<i>°F.</i>	<i>°C.</i>
<i>Noncondensable gases</i>		
Hydrogen	-423	-252.8
Nitrogen	-320	-195.8
Carbon monoxide	-310	-190
Oxygen	-297	-183
<i>Hydrocarbons</i>		
Methane	-259	-161.4
Ethylene *	-155	-104
Ethane	-128	-89
Propylene	-53.7	-47.6
Propane	-44	-42.2
Isobutane	10	-12.2
Isobutylene *	20.1	-6.6
Butylene-1 *	21.0	-6.1
Butadiene-1, 3 †	23.5	-4.7
<i>n</i> -butane	31.1	-0.5
Butylenes-2 *	34 to 38	+1.1 to 3.4
Butadiene-1, 2 †	50.5	10.3
Pentanes and heavier	82.+	28.+

\* In L-P gases from thermally cracked petroleum and in illuminants fraction of manufactured gases.

† Ordinarily not occurring in L-P gases.

begin with Travers,<sup>19</sup> and continues with contributions by Burrell, Seibert, and Robertson,<sup>20</sup> and by Shepherd and Porter.<sup>21</sup> The procedures reach their modern refined state with the extensive work of Podbielniak<sup>22</sup> and others.<sup>23</sup> Tedious and difficult separations requiring much time and considerable skill and patience have given way to the use of almost completely automatic equipment. However, this was only possible after the development of highly efficient distillation columns using controlled reflux and the silvered vacuum jacket for reducing heat leakage from the column.<sup>22</sup>

<sup>19</sup> Travers, M. W., *The Experimental Study of Gases*, Macmillan, N. Y., 1901.

<sup>20</sup> Burrell, G. A., Seibert, F. M., and Robertson, I. W., *Ind. Eng. Chem.*, **7**, 669, 1915; U. S. Bur. Mines Tech. Paper No. 104, 1951.

<sup>21</sup> Shepherd, M., and Porter, F., *Ind. Eng. Chem.*, **15**, 1143, 1923.

<sup>22</sup> Podbielniak, W. J., *Oil and Gas J.*, **27**, No. 35, p. 38, 1929; *Ind. Eng. Chem., Anal. Ed.*, **3**, 177, 1931; **5**, 119, 135, 172, 1933.

NOTE.—One or more of the following patents cover much of the modern low-temperature fractional distillation apparatus. Podbielniak, Inc., Chicago, Ill., is the exclusive licensee.

U. S. Pat. No. 1,909,315

1,917,272

1,935,888

1,967,258

2,009,814

2,088,385

2,093,644

Brit. Pat. No. 380,220

Fr. Pat. No. 721,598

Can. Pat. No. 343,524

Can. Pat. No. 343,525

Rum. Pat. No. 27,009

<sup>23</sup> Frey, F. E., and Yant, W. P., *Ind. Eng. Chem.*, **19**, 492, 1927.

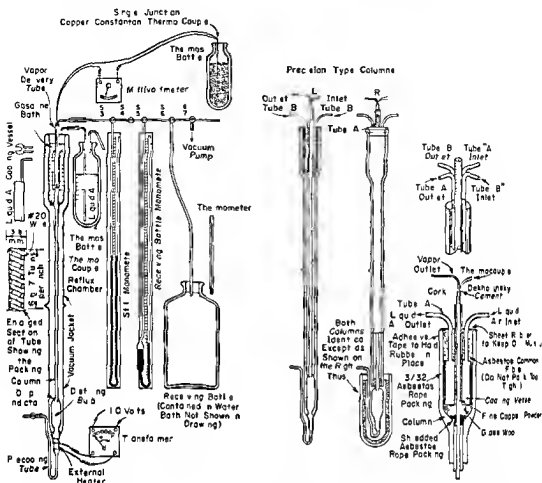


Fig. 3.5. Simple Manual Type Low Temperature Fractionation Apparatus (Copyright 1931 by the American Chemical Society and reproduced with permission of the copyright owner)

Table 35.4 lists the normal boiling points of the lighter hydrocarbons usually encountered in these analyses. The boiling points of some inert and noncondensable gases are also included.

**Apparatus**—The distillation column is a glass tube 3 to 5 mm inside diameter and about 3 ft long. A wire spiral fits the interior of the tube snugly and extends its full length forming the column packing.<sup>24</sup> The column is joined to a short length of slightly larger tube at its top which forms the still head. Sealed into the still head are a metal capillary tube for removing the vaporized fractions and a single junction thermocouple to measure the reflux temperature. A still pot or kettle having a tube for admitting the sample and a small electrical heater is connected to the bottom of the column with a ground glass joint. The size of the kettle depends on the material to be distilled. A capacity of 15 to 25 ml has

<sup>24</sup> Columns developed for special and difficult separations having more efficient packing than the helical wire and known as Super Cool and Super Cal columns use "Hf" Grid packing (See front 22 including patents p. 1525).



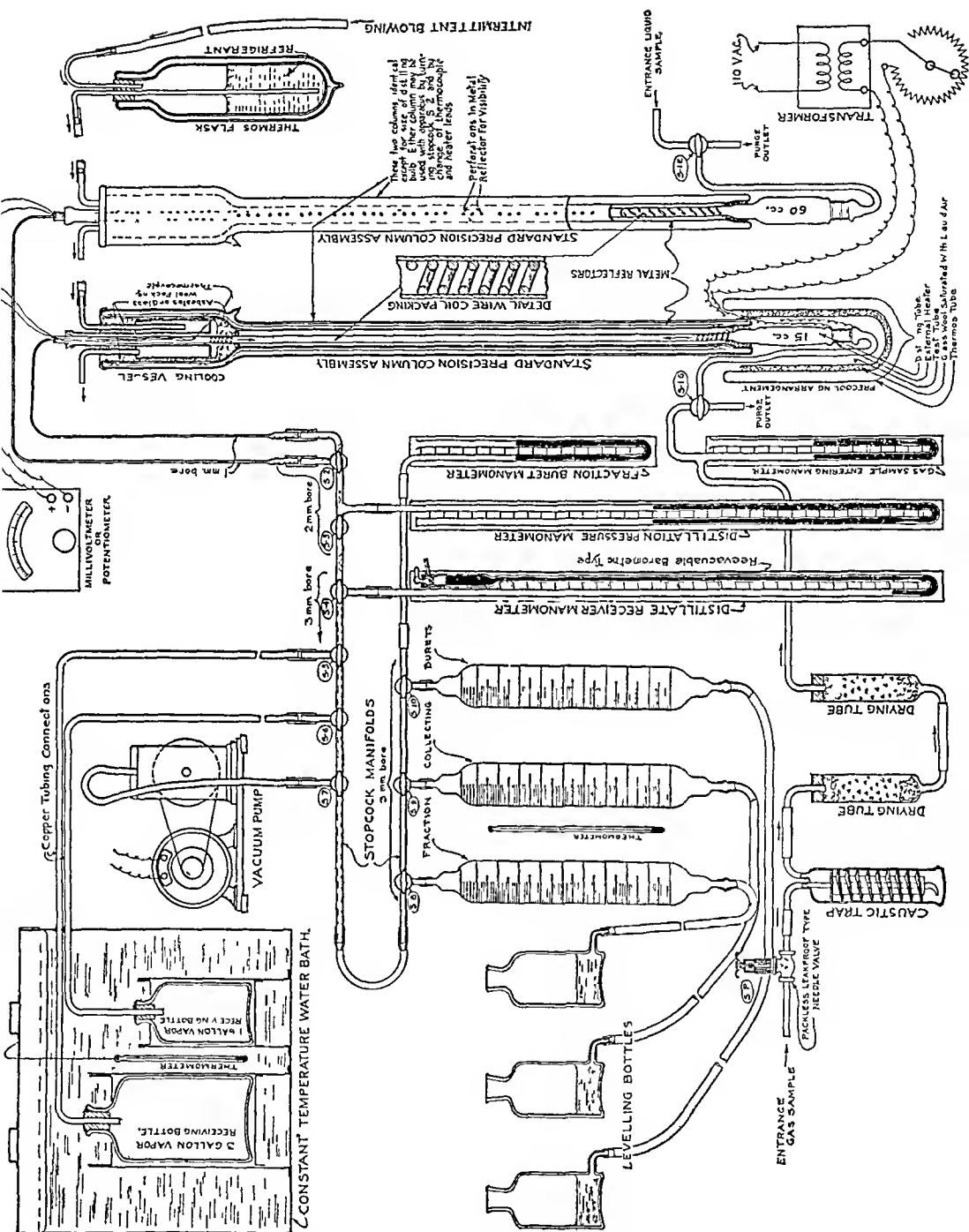


FIG. 35-6. Diagram of Standard Precision Fractionation Apparatus. (Copyright 1933 by the American Chemical Society and reproduced with permission of the copyright owner.)

been recommended for gaseous samples. Larger volumes are used for liquid samples.

A double wall glass evacuated jacket, its interior silvered or provided with metal radiation shields surrounds the still. Its upper portion is enlarged to surround an annular metal cooling vessel which encloses the still head. Vaporization of liquid nitrogen into this cooling vessel cools the column head in turn and produces liquid reflux.

The metal capillary delivery tube is connected to a mercury filled manometer and to a manifold of stopcocks. The manometer registers the column pressure. Manipulation of the stopcocks can close the column in for total reflux, or connect it in turn with each of two or more receiving bottles of equal and known volume used to collect the vaporized fractions. A second mercury manometer indicates the pressure of the gas admitted to each receiver. The reservoir bottles are enclosed in a constant temperature bath.

Reflux temperature which is the equilibrium boiling point of each component as it is removed from the still is indicated on a millivoltmeter or potentiometer or may be displayed on a strip chart recorder.

Auxiliaries include a vacuum pump, Dewar bottles for liquid nitrogen control for the kettle heater and apparatus for removing moisture and carbon dioxide from the sample prior to its entering the column. For the automated models compressed air, a water supply and electric power are also required. Supplementary sample collecting apparatus is sometimes used.

**Procedure**—Gaseous samples are usually supplied under pressure. LPG and some refinery products may be available as liquid samples. In this case they must be handled in such a manner as to assure that a representative sample of vapor is admitted to the distillation apparatus. (See Collection Procedures.) If it is certain that samples are dry and contain no carbon dioxide the purification step may be omitted. Otherwise  $\text{CO}_2$  is removed by Ascarite<sup>25</sup> and moisture by calcium chloride and phosphorus pentoxide as the sample enters the still. The following gives a summary of the steps required for analysis. Reference should however, be made to the operating manual accompanying the particular form of apparatus used. The sequence of operations in detail may vary widely depending on the kind and complexity of the automatic controls provided.

To begin an analysis evacuate the entire apparatus, column, manifold, manometers and receiving bottles. After testing for leaks close the manifold stopcocks for the receiving bottles and blow liquid nitrogen into the cooling compartment of the still head. As the sample is admitted maintain the temperature a little below the normal boiling point of the most volatile hydrocarbon component of the sample. If the sample contains methane and noncondensable gases hold the temperature as low as possible. Chill the still pot to a temperature depending on the volatility of the sample. If some methane is present, a little liquid nitrogen will be required around the still pot initially.

With all receiving bottles closed off by the manifold stopcocks, admit the sample slowly through the inlet at the bottom of the kettle. When the pressure within the still reaches atmospheric, as indicated by the column manometer, adjust the rate of admission and cooling so that liquefaction takes place smoothly without flooding the column, and column pressure remains constant. The condensed liquid

<sup>25</sup> The concentration of  $\text{CO}_2$  in the original sample if required is determined by Ors. analysis.

collects in the still pot. If noncondensibles are present, the column pressure will tend to rise even with adequate cooling. Open very slightly the stopcock connecting the column with the first receiver bottle. Bleed off noncondensibles very slowly to maintain column pressure at atmospheric. If column is flooded, close inlet stopcock and withdraw no gas until the liquid drains into the kettle. Continue admission of sample until kettle is about two-thirds full of liquid. Close outlet stopcock, and block inlet tube and stopcock with a little mercury. Close inlet stopcock. Allow column to come to equilibrium on total reflux, adding nitrogen to the cooling chamber at a rate such that atmospheric pressure is maintained as indicated by the column manometer. The quantity of noncondensibles is indicated by the pressure in the first receiver.

When the reflux temperature has become constant as indicated by the thermocouple, start distillation. Carefully adjust the rheostat controlling heat added to still pot. The stopcock connecting the column to the evacuated receiver which is to collect the first distillate fraction is partially opened. Draw off the most volatile component slowly, balancing kettle heat, reflux cooling, and draw-off rate so that reflux temperature and column pressure remain constant. If column floods because distillation rate is too high, close it in by closing outlet stopcock. Readjust heating rate and allow column equilibrium to be reestablished on total reflux before drawing off more distillate.

When the component being distilled is nearly completely recovered, as indicated by a tendency for reflux temperature to rise, reduce the withdrawal rate. Judicious control of withdrawal rate and cooling will increase the reflux ratio so that very sharp fractionation can be attained with most components.

A very steep temperature rise will occur, indicating that the next most volatile component exists in the reflux compartment. The pressure registered by the receiver manometer indicates the quantity of distillate collected. If fractions are to be collected for further examination, or if receiver pressure approaches atmospheric, close the stopcock to the receiver just filled and open that to the next evacuated bottle. Continue the distillation of each component in turn.

Fractionation of components more volatile than  $C_5$  hydrocarbons is completed at atmospheric pressure. To distill  $C_5$  and heavier, column pressure is reduced to maintain the distillate in vapor form.<sup>26</sup> Distillation of  $C_7$  and higher hydrocarbons is generally considered impractical with this procedure. If the concentration of  $C_5$  and higher is small, as in natural gas, and the still pot and column become nearly dry, these hydrocarbons are drawn off together into an unused evacuated receiver, and reported simply as  $C_5+$ .

Calculation of Composition.—If the reflux temperature during distillation is plotted against the cumulative pressure rise in the receivers (Fig. 35-7), or if it is displayed on a recorder when automatically controlled apparatus is used, a distillation curve showing horizontal sections or "plateaus" is obtained. These correspond to the reflux temperature of each pure component withdrawn. The nearly vertical portions, indicating an abrupt temperature rise as each succeeding component distills are called "breaks," or "break points." The horizontal length of each plateau, between breaks, is proportional to the quantity of the corresponding hydrocarbon present in the sample. The percentage by volume of each component

<sup>26</sup> A maximum distillation pressure of 300 mm. for distilling  $C_5$  hydrocarbons, and 100 mm. for  $C_6$ , is recommended by Denny, L. C., and Luxon, L. L. (ed.), *Handbook of Butane-Propane Gases*, 3rd ed., Jenkins Publications, Los Angeles, 1951.

in the original sample is 100% (pressure increase for component/sum of pressure increase for entire sample in all receivers)

**Supplementary Tests**—Distillate fractions may be recovered from the receiver bottles by auxiliary equipment including a Topley pump for supplementary examination. For example oxygen can be determined in the noncondensable fraction by absorption in pyrogallol. Propane and propylene are not completely separated and are collected together. The unsaturated content of the fraction can also be estimated by volumetric absorption methods. Isomers such as isobutane and butane can be examined by infrared methods.

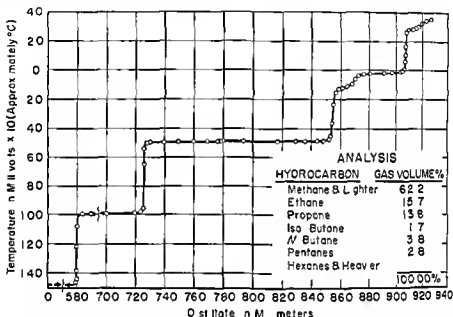


FIG. 35.7 Fractionation Distillation Curve of Natural Gas (Copyright 1931 by the American Chemical Society and reproduced with permission of the copyright owner).

Distillation procedures have also been used with manufactured gases which contain many saturated, unsaturated, and aromatic hydrocarbons. The usual practice is to separate the hydrocarbons into groups having the same number of carbon atoms and determine individual components within these groups by Orsat analysis or additional physical or chemical methods.<sup>2-4</sup>

**Precision of Distillation Analysis**—From the results of cooperative tests among many laboratories conducted by the Natural Gasoline Association of America<sup>2,4</sup> an indication of the reliability of low temperature fractional distillation analysis can be obtained. The major interest here was in natural gasoline analysis and samples were composed of  $C_3$  through  $C_6$  for the most part. The following conclusions may be cited:

The mean deviation from the true value averaged for all components ranged from 0.55 to 1.04 mole per cent for the various types of samples analyzed.

<sup>2</sup> Burke O. W., Starr C. E. and Tuemmler T. D. (ed.) *Light Hydrocarbon Analysis*, Reinhold Publishing Co. N. Y. 1951.

<sup>3</sup> Robey R. F. and Wiese H. K. *Ind. Eng. Chem. Anal. Ed.* 20, 926, 1948.

<sup>4</sup> Miller A. J. *Petroleum Engineer* p. C 31, Aug. 1952.

"Major errors are not due to basic procedures or apparatus and are attributed to human element factors . . ."

Another reported examination of the distillation procedure attempted to evaluate modifications and special tests for complete analysis of complex  $C_3 + C_4 + C_5$  samples.<sup>27</sup> The conclusion was drawn here that ". . . On the average, a given laboratory can be expected to make determinations for most light hydrocarbon components of a gas within a probable error of  $\pm 0.2$  to  $0.3$  mole per cent. Furthermore, the extent to which laboratories check each other has been found to be within values two to three times the probable error for a given laboratory." And ". . . Distillation and mass spectrometer methods show about the same accuracy and precision for the analysis of total  $C_3$ , total  $C_4$ , and total  $C_5$ ."

Analyses of natural gases are at times used to calculate the heating value of the fuel. Agreement between calculated and carefully measured heating values may be used, with some caution, as an index of the accuracy of the analyses. In the author's laboratory, the heating values of upward of a hundred natural gas samples have been calculated from low-temperature fractional distillation analyses. The range of composition was narrow; the heating values varied only between 1020 and 1150 Btu per cubic foot. Experimentally determined values were obtained at the time of sampling with a carefully adjusted and calibrated Thomas calorimeter. It was found that the average difference between calculated and experimental results was about 3 Btu per cubic foot.

### ANALYSIS BY MASS SPECTROMETER

The use of the mass spectrometer for the analysis of industrially important gases has undergone intensive development in the past two decades, largely by the petroleum industry. Commercially available instruments are now capable of rapid analysis of complex mixtures of hydrocarbons and other components found in fuel gases and related materials with a facility unattainable by other means. However, because of the relatively large initial investment required for the mass spectrometer and the ancillary equipment, their expense can be justified only by full and continuous utilization of such facilities. Moreover, they are never fully shut down except for major maintenance, and a trained crew must be constantly available for their operation. Thus they are ordinarily limited to those organizations requiring numerous and regular analyses of products and process streams, the value of which can support the cost of the equipment. Chemical and petroleum processing companies, and certain research and analytical agencies are among these.

Mass spectrometers manufactured by the Consolidated Engineering Company, General Electric Company, and Westinghouse (Research model) have been satisfactorily used for gas analyses. The components which may be determined are shown in Table 35-5, for natural gases and carburetted water gas. More complex mixtures, such as manufactured "oil gas," have also been analyzed by these procedures with success. Many analyses of hydrocarbon streams in refineries are run routinely by mass spectrometer.

The basis of separation and recognition of the molecular species making up a gaseous mixture is in their dissociation and ionization, by electron bombardment at very low pressure, to produce positive ions of different masses. The ions are first accelerated by an electric field, then separated by causing them to take circular paths, with radii depending on the ratio,  $m/e$ , of mass to charge, between the poles of an electromagnet. Light ions travel in paths of short radius, while heavier ions

TABLE 35-5 COMPONENTS DETERMINABLE BY MASS SPECTROMETRIC ANALYSIS

<i>In Natural Gases</i>	<i>In Carburetted Water Gas</i>
Helium	Hydrogen
Neon	Oxygen
Argon	Nitrogen
Oxygen	Carbon monoxide
Nitrogen	Carbon dioxide
Carbon dioxide	Hydrogen sulfide
Hydrogen sulfide	Methane
Sulfur dioxide	Ethane
Methane	Ethene
Ethane	Propane
Ethene	Propene
Propane	Isobutane
Propene	Butane
Isobutane	Butenes
Butane	Pentanes
Butenes	Pentenes
Pentanes	Hexane
Pentenes	Butadiene
Hexane	Carbon disulfide
	Benzene
	Toluene
	Xylene
	Styrene
	Naphthalene

take paths of larger radius. An ion collector is provided to collect the ions of different masses separately as the accelerating potential or magnetic field is changed to bring them to the collecting target. A quantitative measure of the ions collected is provided by the magnitude of the voltage developed at the target by the ions discharged. The instrument thus produces a mass spectrum of the different ions formed in the gas or mixture being analyzed. When displayed on a recorder chart the record takes the form of a horizontal base line with peaks at intervals corresponding to masses of the different ionized molecules or molecular fragments produced in the ionization chamber. The height of the peaks represents the ion voltage and hence the abundance of ions of each type formed. Different molecular species produce unique mass spectra, so that the resolution of a complex record gives information from which the composition of the mixture can be estimated.

The mass spectrometer must be calibrated periodically with pure samples of each of the individual components to be determined in a mixture. Then by using the mixture spectrogram and the spectrograms obtained in the calibration procedure the composition of the mixture is determined by solving a system of linear simultaneous equations.

Detailed instructions and procedures for operation and maintenance of the different available models of mass spectrometers are provided by the manufacturer. They are beyond the scope of this discussion. General instructions pertinent to the adjustment, calibration and use of mass spectrometers are to be found in the ASTM Standard Methods noted below.

Analysis of natural gas with the mass spectrometer may be made according to ASTM Standard Method D1137-53.<sup>30</sup> This method is intended for the determination of the complete chemical analysis of natural gases or similar gaseous mixtures through the  $C_4$  hydrocarbons. A Tentative Method D1302-53<sup>31</sup> is proposed for the analysis of carburetted water gas and similar gaseous mixtures. The development of these standardized procedures, and the appraisal of their reliability was the result of a cooperative investigation made by the National Bureau of Standards, the American Society for Testing and Materials, and a large number of analytical laboratories.<sup>32, 33</sup>

The accuracy and the reproducibility of mass spectrometric analyses of gases depends somewhat on the complexity of the mixture to be analyzed, on the ability of the analyst to identify all components to be accounted for, and the care used in calibration. Necessary skill in operation and maintenance of the instrument, already referred to, requires extensive experience. Shepherd<sup>32, 33</sup> has given estimates of probable accuracy and reproducibility of analyses of a natural gas sample studied in the extensive cooperative test. His data are shown in Table 35-6 and

TABLE 35-6. PRECISION AND ACCURACY OF MASS SPECTROMETER ANALYSES WITH NATURAL GAS

Gas	Probable Accuracy	Reproducibility	
		Different Laboratories and Apparatus	One Laboratory and Apparatus
Methane, %	1.0 to 0.5	0.5	0.2
Ethane, %	0.5	0.3	0.1
Propane, %	0.1	0.06	0.02
Propene, %	0.5 to 0.2	0.04	0.02
CO <sub>2</sub> , %	0.1	0.03	0.02
Nitrogen, %	1.0	0.3	0.2
Calculated heating value, %	1.0	0.5	0.2
Specific gravity, %	0.6	0.6	0.2

NOTE: The data in Table 35-6 are based on extensive cooperative work on a standard gas mixture. Allowance has been made for the fact that many mixtures encountered industrially may be more difficult to resolve than the standard mixture studied.

indicate that an accuracy equivalent to or better than low-temperature distillation and volumetric gas analysis methods can be expected.

Mass spectrometric methods have the ability to separate all components of the "illuminant" and paraffin fractions of complex fuel gases. This is in contrast with the very limited separations obtained in even the most refined volumetric procedures.

<sup>30</sup> Standard Method for Analysis of Natural Gases and Related Types of Gaseous Mixtures by the Mass Spectrometer, D1137-53, A.S.T.M. Standards, Part 8, American Society for Testing and Materials, Philadelphia, Pa., p. 1224, 1958.

<sup>31</sup> Tentative Method for Analysis of Carburetted Water Gas by the Mass Spectrometer, D1302-53T, ASTM Standards, Part 8, American Society for Testing and Materials Philadelphia, Pa., p. 1299, 1958.

<sup>32</sup> Shepherd, M., *BS Journal of Research*, **38**, 19, 1947. RP 1759.

<sup>33</sup> Shepherd, M., *BS Journal of Research*, **44**, 509, 1950. RP 2098.

**Sample Preparation.**—Any appreciable hydrogen sulfide content should be removed by connecting a tube of Ascarite ahead of the sample container during sampling or ahead of the drying tube when entering the sample into the chromatograph. This also removes carbon dioxide, and the results obtained will be on the acid gas free basis.<sup>37</sup>

Connect the sample container outlet valve to chromatograph sample valve using a minimum of connecting line. Mount a dryer between the sample container and the chromatograph sampling valve unless the sample is known to be free of water vapor. Use metal or short pieces of Tygon for connections. Do not use rubber tubing. All lines, valves and connections must be clean and dry.

Open the sample cylinder outlet valve and purge the sample through the entry system and sample holder.<sup>38</sup> Pass the outlet from the sample holder through a tube extended just below the surface of a container of water to indicate the rate of sample flow. Adjust the flow to one or two bubbles per second. Flush for three minutes or more. Adjust the recorder base line to coincide with the recorder zero. Manipulate the sample valve to enter the sample.

**Partition Column Run for Ethane and Heavier Hydrocarbons and CO<sub>2</sub>.**—Usually a 1 to 3 ml. sample will be satisfactory for most gases. If the gas is lean, a 5 ml. sample may be needed for good measurements of low-concentration components, particularly C<sub>6</sub>+. Enter the sample and obtain a chromatogram through *n* pentane and reverse the carrier flow. Adjust the attenuator at each peak for maximum peak height within recorder chart range. The run is complete after the back-flush peak is obtained, as evidenced by the recorder pen returning to and remaining on the base line. Obtain a corresponding chromatogram on the reference standard. The reference standard run is complete after the elution of *n* pentane.

Methane may also be determined on this column if the column used will separate it from nitrogen and oxygen (i.e., silicone 200/500) and if the sample size does not exceed 0.3 ml.

**Molecular Sieves Column Run for Oxygen, Nitrogen, and Methane.**—The sample size must not exceed 0.3 ml. for the determination of methane. Enter the sample and obtain a chromatogram through methane. Reverse the carrier flow to clean the column by back-flush. Likewise obtain a chromatogram showing nitrogen and methane on the reference standard. Obtain a chromatogram on dry air showing oxygen and nitrogen if oxygen is to be determined. The air may be entered at an accurately measured reduced pressure or from a helium diluted mixture.

**Molecular Sieves Column Run for Helium.**—This run is made using nitrogen or argon as the carrier gas. Enter a 3- to 5-ml. sample (large enough to obtain a good measurable helium peak). The helium peak will be just ahead of oxygen and will be obtained in about two minutes using about 5 psig carrier pressure at the column inlet. Reverse the carrier flow after helium to clean the column. Obtain a corresponding chromatogram on a reference standard containing a suitable percentage of helium.

<sup>37</sup> Hydrogen sulfide content in the order of 10 grains or less per 100 scf will have negligible effect on concentrations of other components and need not be removed if all materials contacting the sample are inert to hydrogen sulfide. If Ascarite tube is used, the concentration of H<sub>2</sub>S and CO<sub>2</sub> should be determined when sample is collected.

<sup>38</sup> If the possibility exists that hydrocarbon condensation in the sample cylinder could occur, the cylinder should be heated above the collection temperature until reevaporization is complete and during sample admission.



**Sample Preparation.**—Any appreciable hydrogen sulfide content should be removed by connecting a tube of Ascarite ahead of the sample container during sampling or ahead of the drying tube when entering the sample into the chromatograph. This also removes carbon dioxide, and the results obtained will be on the acid gas free basis<sup>37</sup>

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**Partition Column Run for Ethane and Heavier Hydrocarbons and CO<sub>2</sub>.**—Usually a 1 to 3 ml sample will be satisfactory for most gases. If the gas is lean, a 5 ml sample may be needed for good measurements of low concentration components, particularly C<sub>6</sub>+. Enter the sample and obtain a chromatogram through *n* pentane and reverse the carrier flow. Adjust the attenuator at each peak for maximum peak height within recorder chart range. The run is complete after the back flush peak is obtained, as evidenced by the recorder pen returning to and remaining on the base line. Obtain a corresponding chromatogram on the reference standard. The reference standard run is complete after the elution of *n* pentane.

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<sup>37</sup> Hydrogen sulfide content in the order of 10 grains or less per 100 scf will have negligible effect on concentrations of other components and need not be removed if all materials contacting the sample are inert to hydrogen sulfide. If Ascarite tube is used the concentration of H<sub>2</sub>S and CO<sub>2</sub> should be determined when sample is collected.

<sup>38</sup> If the possibility exists that hydrocarbon condensation in the sample cylinder could occur, the cylinder should be heated above the collection temperature until reevaporation is complete and during sample admission.

The heights of the peaks produced on the recorder chart for each component are measured and compared with the peak heights for the corresponding components on the calibration record for the standard reference mixture made at the same time. The mole percentage of each component in the unknown is calculated with the expression

$$C = \frac{A}{B} \times S,$$

where  $C$  = mole per cent of component in sample,

$A$  = peak height of component in sample, mm,

$B$  = peak height of component in standard, mm,

$S$  = mole per cent of component in standard

For hexanes and heavier components using columns and conditions as specified the peaks are too broad for satisfactory use of peak heights. The areas under the curve in the back flushing step between peaks and base line are therefore employed.

**Precision of Analysis**—Chromatographic methods are still undergoing development especially with respect to column materials and operating conditions. It is therefore difficult to appraise reliably the precision attainable with these techniques. However the following estimate given by the N G A A for its tentative standard method may be used as a guide for natural gas analyses made on the same sample by different laboratories

<i>Component mol %</i>	<i>Single Component Reproducibility</i>	<i>Group C<sub>6</sub> + Reproducibility</i>
0-1	03	10% of amount
1-5	05	10% of amount
5-25	10	
over 25	30	

The N G A A procedure<sup>39</sup> describes the method in somewhat greater detail including recommendations for preparation of the columns, procedures for supplementary and partial analyses, and several helpful precautionary measures.

Similar procedures have been applied in the analysis of liquefied petroleum gases and to reformed natural gas when suitable reference standard mixtures are available. In sampling the LPG for analysis the precautions necessary for obtaining a representative sample in gaseous form must be adhered to if the unknown or reference standard are in the liquid state.

Reformed natural gas contains substantial proportions of hydrogen, carbon monoxide, and carbon dioxide. However since hydrocarbons heavier than methane are not likely to be present, adsorption columns only are used. For example a silica gel column at 40°C is suggested for CO<sub>2</sub>. A second run with a molecular sieves column at 35°C will separate the oxygen, nitrogen, carbon monoxide, and methane. Helium is used as carrier gas. To determine hydrogen the molecular sieves column is again used, but nitrogen must be employed as carrier because of the relative thermal conductivities of hydrogen and helium.

Gas chromatographic techniques are advancing rapidly, and many are primarily useful for research purposes. Further standardization of procedures are, however, receiving extensive attention.

<sup>39</sup> Tentative Method for Natural Gas Analysis by Gas Chromatography, Natural Gas Association of America, Tulsa, Okla., 1961.

## DETERMINATION OF MISCELLANEOUS CONSTITUENTS

## HYDROGEN SULFIDE

Hydrogen sulfide,  $H_2S$ , is encountered in utility fuel gases manufactured from coal or by pyrolysis of sulfur-bearing oils. Liquefied gases from petroleum refining processes may contain small amounts, but the purified marketable product is substantially free of it. It occurs in natural gases only from certain localities. Its concentration in this "sour" gas may be as much as 20%, and it can cause extensive corrosion damage to castings and processing equipment. Natural gas as distributed to consumers rarely contains more than a minute trace, if any, hydrogen sulfide.

NOTE.—Hydrogen sulfide is nearly as toxic as HCN, and its action may be as rapid. It is a noncumulative poison, is rapidly oxidized by the blood, and its products are non-toxic; 0.01 to 0.015% may produce death in from 8 to 48 hours if breathed continuously. Concentrations of 0.05 to 0.07% are dangerous, and 0.1 to 0.3% rapidly fatal.

Methods selected for detection and determination of hydrogen sulfide will depend on the purpose of the analysis, the concentration present, and the accuracy desired.

## LEAD ACETATE PAPER TEST

A quick qualitative test for the presence of hydrogen sulfide makes use of moistened lead acetate paper. If a strip of filter paper wetted with 5% lead acetate solution is held in the gas stream, the speed with which a brown or black coloration develops may be used as a rough estimate of the  $H_2S$  present. The procedure can be made semi-quantitative in the following way.<sup>40,41</sup>

*Apparatus.*—A glass cylinder 1.75 in. in diameter by 8 in. long; bottom stopper fitted with a gas inlet tube and glass baffle 1 to 1.25 in. diameter; top stopper fitted with a 5-cu. ft. per hour gas burner at outlet and glass suspension hook arranged as in the diagram in Fig. 35-8.

*Procedure.*—Dip a strip of white filter paper, 2 in. wide by 6 in. long, in a 5% lead acetate solution; press the strip between clean blotters to remove excess solution; immediately suspend the strip so that it is midway between the baffle and upper stopper and pass gas at 4.5 to 5.5 cu. ft. per hour for 1 minute. Immediately compare the exposed strip with another strip moistened with the same solution but not exposed to the gas. If the exposed strip is not distinctly darker, the gas is considered free from hydrogen sulfide.

*Sensitivity.*—The limit of detection is 0.3 to 0.4 grains  $H_2S$  per 100 cu. ft. of gas for tests of 1-minute exposure. The duration of the test can be varied, keeping other conditions the same. With 30 seconds exposure the minimum detectable concentration is about 0.45 grain per 100 cu. ft. of gas, or with a 30-minute test, about 0.2 grain. Factors influencing the test are paper surface, opacity, moisture content and method of preparation, strength of lead acetate solution, exposure time, gas flow rate, size of apparatus.

## TUTWILER DETERMINATION

This method has been extensively used as a control test in gas-manufacturing and coke-oven plants for instantaneous determinations on gas containing 10 grains of  $H_2S$  or more per 100 cu. ft. of gas. The gas sample is drawn into a special pipet,

<sup>40</sup> McBride, R. S., and Edwards, J. D., NBS Technologic Paper, No. 41, 1914.

<sup>41</sup> NBS Circular No. 48, Standard Methods of Gas Testing, 2nd ed., 1916.

starch solution added and the hydrogen sulfide titrated directly with standard iodine solution

**Apparatus**—A 100 ml capacity Fawcett buret with a two way glass stopcock at the bottom and a three way stopcock at the top connecting either with an inlet tube or a glass stoppered cylinder 10 ml capacity graduated in 0.1 ml subdivisions with rubber tubing connecting the buret with a leveling bottle with a

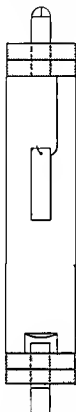


FIG 35 8 Test for Hydrogen Sulfide with Lead Acetate Paper (Reproduced with permission from V J Allen's Gas Analysis and Testing of Gaseous Materials American Gas Assn New York 1945)

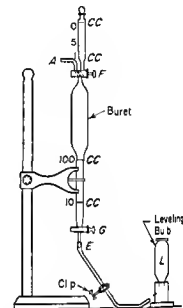


FIG 35 9 Fawcett Buret (Reproduced with permission from V J Allen's Gas Analysis and Testing of Gaseous Materials American Gas Assn New York 1945)

clump for closing off the rubber tubing all assembled on a stand as shown in Fig 35 9

**Reagents** Iodine Stock Solution 0.1 N—Weigh 12.7 g of iodine and 20 to 25 g of c.p. potassium iodide for each liter of solution. Dissolve the KI in as little water as possible, dissolve the iodine in the concentrated KI solution, make up the proper volume with distilled water and store in a glass stoppered brown glass bottle.

**Standard Iodine Solution, 1 ml = 0.00171 g I**—Transfer 33.7 ml of the above 0.1 N stock solution into a 250 ml volumetric flask, add water to the mark and mix well. Then

$$1 \text{ ml} = 0.00171 \text{ g I} = 100 \text{ grains H}_2\text{S per 100 cu ft of gas}$$

**Starch Solution.**—Shake about 5 g. of soluble starch with 100 ml. of water; pour into 1 liter of boiling water; stir; let cool and decant off the clear starch solution. Make a fresh solution every few days.

**Procedure.**—Fill the leveling bottle, *L*, with starch solution. Raise *L*, open cock *G*, open *F* to *A*, and close *F* when the solution starts to run out of gas inlet tube *A*. Close *G*. Purge the gas sampling line and connect it with *A*. Lower *L* and open *F* and *G*. When the liquid level is several ml. past the 100-ml. mark, close *G* and *F*, and disconnect the sampling tube at *A*. Open *G* and bring the starch solution to the 100-ml. mark by raising *L*; then close *G*. Open *F* momentarily to bring the gas in the buret to atmospheric pressure, and close *F*. Open *G*, bring the liquid level down to the 10-ml. mark by lowering *L*. Close *G*, clamp the rubber tubing near *E* and disconnect it from the buret. Rinse the graduated cylinder twice with standard iodine solution (0.00171 g. I per ml.); fill the cylinder and record the reading. Introduce successive small amounts of iodine through *F*, shake well after each addition, and continue until a faint, permanent blue color is obtained. Record the reading, subtract the initial reading, and call the difference *D*.

With every fresh stock of starch solution perform a blank test as follows: Introduce fresh starch solution into the buret up to the 100-ml. mark. Close *F* and *G*. Lower *L* and open *G*. When the liquid level reaches the 10-ml. mark, close *G*. With air in the buret, titrate in the same way as during a test and up to the same end point. Call the ml. of iodine used *C*. Then

$$\text{Concentration of H}_2\text{S, grains/100 cu. ft.} = 100(D - C).$$

The test may be modified for use with smaller concentrations of  $\text{H}_2\text{S}$ , by using a similar buret of 500-ml. capacity and a more dilute (.001 *N*) iodine solution. The manipulation is the same as described for using the 100-ml. buret. The test as modified is sufficiently sensitive that concentrations of hydrogen sulfide less than 1.0 grain per 100 cu. ft. can be determined. Since the starch-iodine end point is less distinct with the dilute reagent, it is recommended that the end point be compared with that determined when a sample of  $\text{H}_2\text{S}$ -free air is titrated in the same buret. The quantity of iodine solution required to produce the end point color in the blank determination is subtracted from the total reagent consumed in the actual test.

#### U. S. STEEL CHEMISTS' METHOD <sup>42</sup>

If an average analysis for hydrogen sulfide in a gas stream is required over an extended period, consideration should be given to the preference of collecting an average sample of gas or of carrying out a continuous analysis for the constituent. In the former case the average  $\text{H}_2\text{S}$  concentration can be determined at the end of the collection period by a Tutweiler buret procedure. However, there is almost inevitably a loss of  $\text{H}_2\text{S}$  by reaction with the container material or the confining fluid. Therefore, a procedure in which gas is passed slowly through a reagent which will remove the hydrogen sulfide quantitatively is usually preferable. Sample size can be adjusted by the flow rate and total collection time, and can be determined by a suitable meter following the absorption train. Such a procedure will also lend itself to the determination of very small concentrations of  $\text{H}_2\text{S}$  by using a suitably large gas sample.

<sup>42</sup> Methods of Chemists of the U. S. Steel Corporation for the Sampling and Analysis of Gases. Carnegie Steel Co., Pittsburgh, Pa., 1927.

The U. S. Steel Chemists Method<sup>40, 43</sup> is one of several adaptations of this procedure. It involves passing a metered sample of gas through a potassium or sodium hydroxide solution or through an ammoniacal solution of cadmium chloride or zinc sulfate acidifying with hydrochloric acid and titrating the liberated hydrogen sulfide with standard iodine or iodate solution.

**Apparatus**—A Mulligan gas washing bottle or two ordinary gas washing bottles, each carrying a gas inlet bubbling tube and a gas outlet tube, a wet test meter, sulfur free tubing, gas sample line and connections.

**Reagents** **Starch Indicator**—Shake 6 g of soluble starch with 100 ml cold water, add to 1 liter of boiling water, boil 5 minutes, cool, add 6 g zinc chloride dissolved in 50 ml cold water (as a preservative), mix well, let stand 24 hours with occasional shaking, decant the supernatant liquid into a glass stoppered bottle, add 3 g potassium iodide and dissolve.

**Ammoniacal Cadmium Chloride Solution**—Dissolve 5 g cadmium chloride in 375 ml water and add 625 ml of concentrated ammonium hydroxide.

**Ammoniacal Zinc Sulfate Solution**—Add 10 g zinc sulfate to 50 ml concentrated ammonium hydroxide in a 1000 ml volumetric flask, stir, make up to 1 liter with distilled water.

**Sodium or Potassium Hydroxide Solution**—Dissolve 20 g of sodium or potassium hydroxide in 1 liter of water.

**Standard 0.1 N Potassium Iodate Solution**—To a 1000 ml volumetric flask add 3.57 g potassium iodate, 13.8 g potassium iodide and 300 ml water, shake well, add 1 g potassium hydroxide, shake until dissolved, add water to make 1 liter of solution.

**Standard 0.1 N Iodine Solution**—Transfer 12.7 g iodine and 18 g potassium iodide to a 1 liter volumetric flask, add about 50 ml cold water, shake well, dilute to 1 liter, let stand 24 hours before standardizing.

**Procedure**—Into the gas washing bottle place 20 ml of the selected absorbent solution, add about 200 ml water and mix well. Purge the gas sampling line and connect with the gas inlet tube. Connect the gas outlet tube with the meter<sup>44</sup> and pass about 0.1 cu ft of gas through the absorbent. The total gas volume and sampling time can be varied depending on the estimated concentration of H<sub>2</sub>S in the gas. The rate of flow of the sample through the absorbers should not exceed about 100 ml per minute. Record the sample volume, meter temperature and pressure, and the barometric pressure.

Disconnect the flask. Wash the bubbling tube with about 100 ml of water containing 1 to 2 ml of 1:1 hydrochloric acid, add about 5 ml starch indicator, add an excess of 1:1 hydrochloric acid and immediately titrate the liberated hydrogen sulfide with standard 0.1 N iodine or iodate solution, adding the standard solution rapidly at first with little shaking to avoid loss of H<sub>2</sub>S. Let  $D$  represent the ml of titrating standard solution used. Then

$$G = \frac{(D)(0.0273)(100)}{V} = \frac{2.63D}{V} \text{ and}$$

$$H = G/636.4,$$

<sup>43</sup> Miller, A. J. *Gas Analysis and Testing of Gaseous Materials*. American Gas Association, N. Y., 1945.

<sup>44</sup> When using an ammoniacal solution, insert between the absorber and meter a second gas scrubbing bottle containing 5% sulfuric acid solution to absorb ammonia vapor.

where  $G$  = grains  $H_2S$  per 100 cu. ft. of gas,

$H$  = volume per cent of  $H_2S$  in the entering gas,

$V$  = volume of gas registered by the meter, corrected first to standard conditions (60°F., 30.0 in. Hg, saturated) and then for concentration of  $CO_2$  in inlet gas which is absorbed with the  $H_2S$ ,

0.0273 = grain of  $H_2S$  equivalent to 1 ml. of 0.1  $N$  iodine solution.

### OTHER METHODS

Shaw<sup>45</sup> has described a method for the rapid determination of hydrogen sulfide and mercaptans in gases containing only a few grains of sulfur compounds per hundred cubic feet of gas. A special glass flask is required, in which both absorption of the  $H_2S$  in cadmium chloride solution, and titration with standard iodine solution take place.

For determination of  $H_2S$  in extremely minute concentrations, colorimetric methods have been devised. Probably the most reliable are the methylene blue method developed at the Bureau of Mines,<sup>46</sup> and the bismuth sulfide method of Field and Oldach.<sup>47</sup>

### ORGANIC AND TOTAL SULFUR

Sulfur occurring in fuel gases, other than that found as hydrogen sulfide, is classified generally as "organic sulfur." The variety of compounds containing both sulfur and carbon are usually determined as a group, without distinguishing the nature of the different organic residues. If any small residual quantity of hydrogen sulfide is also included, the results of such determination are expressed as "total sulfur." The quantities normally encountered in such determinations with manufactured or natural gases will rarely exceed 50 grains of sulfur per 100 cu. ft. of gas. The principal sulfur-bearing molecules will be carbon disulfide,  $CS_2$ ; carbon oxysulfide (carbonyl sulfide),  $COS$ , thiophene, and mercaptans in coke-oven and other manufactured gases. Natural gases and refinery gas streams, including liquefied petroleum gases, may contain mercaptans,  $RSH$ ,<sup>48</sup> sulfides,  $R-S-R$ , and disulfides,  $R-S-S-R$ .

The older Referee test,<sup>49,50</sup> long used by the gas manufacturing industry for organic or total sulfur determinations, has been superseded in modern analytical practice by two procedures adopted by the American Society for Testing and Materials. The Standard Method, D1072-56,<sup>51</sup> Total Sulfur in Fuel Gases, may be used for any kind of utility fuel gas, including liquefied petroleum gases as distributed in their gaseous form. The Tentative Method, D1266-59T,<sup>52</sup> for sulfur in liquid petroleum fractions, is useful for samples of LPG when collected in the liquid state.

<sup>45</sup> Shaw, J. A., *Ind. Eng. Chem., Anal. Ed.*, **8**, 162, 1936.

<sup>46</sup> Sands, A. E., Grafins, M. A., Wainwright, H. W., and Wilson, M. W., U. S. Bureau of Mines, R.I. 4547, 1949.

<sup>47</sup> Field, E., and Oldach, C. S., *Ind. Eng. Chem., Anal. Ed.*, **18**, 665, 1946.

<sup>48</sup> R stands for an organic, or carbon-containing radicle.

<sup>49</sup> Altieri, V. J., *Gas Analysis and Testing of Gaseous Materials*, American Gas Association, N. Y., 1945.

<sup>50</sup> N.B.S. Circular No. 48, *Standard Methods of Gas Testing*, 2nd ed., 1916.

<sup>51</sup> Standard Method of Test for Total Sulfur in Fuel Gases, D1072-56, A.S.T.M. Standards, Part 8, p. 1211, American Society for Testing and Materials, Philadelphia, Pa., 1958.

<sup>52</sup> Tentative Method of Test for Sulfur in Petroleum Products Including Liquefied Petroleum Gas by Lamp Combustion, D1266-57T, ASTM Standards, Part 8, p. 1279, American Society for Testing and Materials, Philadelphia, Pa., 1958.

## TOTAL SULFUR IN FUEL GASES

This method is intended for the determination of total sulfur in fuel gases at concentrations between 10 and 30 grains of sulfur per 100 cu ft. It is applicable to natural gases, manufactured gases, and mixed gases.

A metered sample of gas is burned in a closed system in an atmosphere of sulfur-free air. The oxides of sulfur produced are absorbed in sodium carbonate

solution wherein they are oxidized to sulfate. The sulfate in the absorbent solution is subsequently determined by titration with standard barium chloride solution using tetrathion quinone as an indicator.

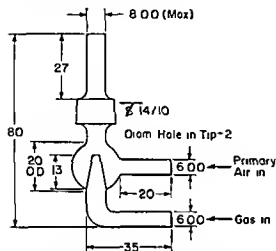
The following description of the method is adapted from ASTM Standard Method D1072-56.

**Apparatus**—The apparatus consists of the following:

**Burner** (Fig. 35-10) of Pyrex Glass.

**Chimneys, Absorbers, and Spray Traps** Indicated in Fig. 35-11.

**Flow Meter**—A calibrated capillary flowmeter for predetermining and indicating the rate of flow of gas to the burner. The capillary selected should be of such size that at the required rate of flow the differential pressure is at least 20 cm of water. A scale divided into millimeters will then provide a reading precision of  $\pm 0.5\%$ .



Note—All dimensions in millimeters.

Fig. 35-10 Burner for Total Sulfur Apparatus. Reproduced with permission from ASTM Standards, ASTM, Philadelphia, 1958.

Other metering devices such as a rotameter or a dry displacement meter will be suitable if the precision of reading the scale is equivalent. A flow controlling valve is attached to the inlet connection of the flowmeter.

**Vacuum System**—A vacuum manifold equipped with a vacuum regulating device, valves, etc. A convenient arrangement for multiple tests is shown in Fig. 35-12, but any other similar system may be used. A flow of about 3 l per minute of air is required through each absorber. A constant manifold pressure of approximately 40 cm of water below atmospheric is maintained.

**Air Purifying System**—A device to supply purified air to the burner manifold at a nearly constant pressure of approximately 20 cm of water, and to the chimney manifold at a pressure of 1 to 2 cm of water is illustrated in Fig. 35-13. But any other similar system may be used.

**Manometer**—A water manometer for indicating the gas pressure at the point of volume measurement. It is connected between the flowmeter and the burner with one leg open to the atmosphere.

#### Reagents and Materials

**Alcohol**—Ethyl alcohol denatured by Formula 30 or 3A or isopropyl alcohol.

**Standard Barium Chloride Solution (1 ml = 1 mg S)**—Dissolve 7.634 g of cp  $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$  in water and dilute to 1 liter. Standardize the solution gravimetrically by precipitation as barium sulfate.



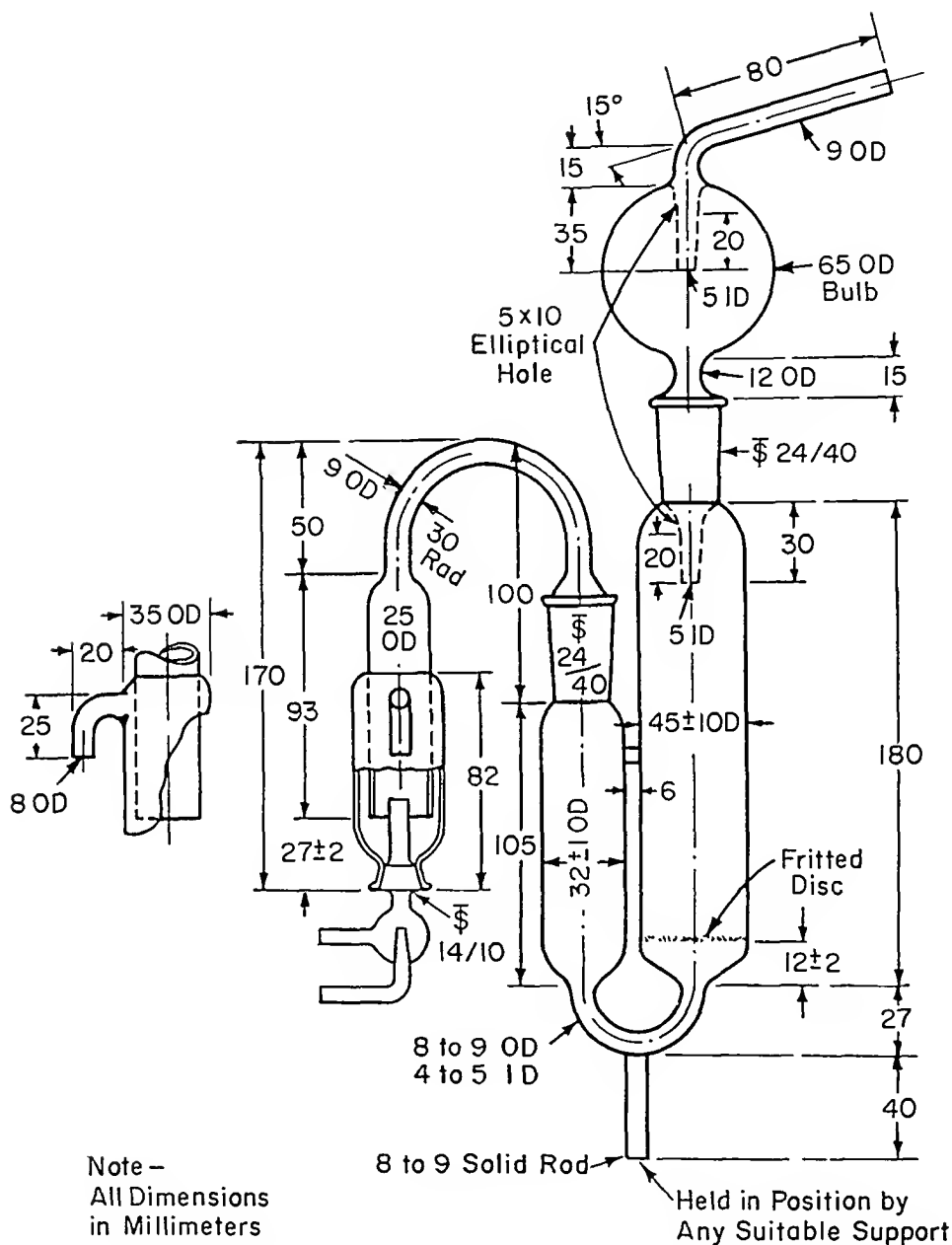


FIG. 35-11. Total Sulfur Lamp. (Reproduced with permission from ASTM Standards, ASTM, Philadelphia, 1958.)

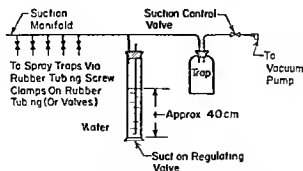


FIG. 35.12 Suction System (Reproduced with permission from ASTM Standards ASTM Philadelphia 1958)

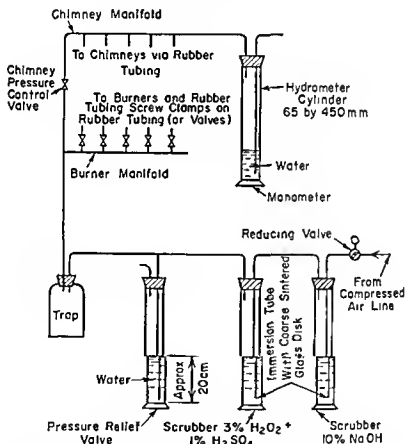


FIG. 35.13 Purified Air System for Multiple Determinations (Reproduced with permission from ASTM Standards ASTM Philadelphia 1958)

Hydrochloric Acid (2.275 g. HCl per liter).—Compare this solution by titration with the  $\text{Na}_2\text{CO}_3$  solution, using methyl orange indicator. Adjust, if necessary, so that 1 ml. of HCl solution is equivalent to 1 ml. of  $\text{Na}_2\text{CO}_3$  solution.

Hydrogen Peroxide, (30%).

Methyl Orange Indicator Solution.—Dissolve 0.1 g. methyl orange in 100 ml. water.

Silver Nitrate Solution (17 g.  $\text{AgNO}_3$  in 100 ml. of water).—Keep in a brown bottle.

Sodium Carbonate Solution (3.306 g.  $\text{Na}_2\text{CO}_3$  per liter).—Dissolve 3.306 g. of  $\text{Na}_2\text{CO}_3$  in water and dilute to 1 liter.

Sodium Hydroxide Solution (100 g. NaOH per liter).—Dissolve 100 g. of technical grade NaOH pellets in water and dilute to 1 liter.

Sulfuric Acid (1:16).—Mix 60 ml. of  $\text{H}_2\text{SO}_4$  (sp. gr. 1.84) with 960 ml. of water.

Tetrahydroxyquinone Indicator (THQ), in powdered form.<sup>53</sup>

*Preparation of Apparatus.*—Place 300 to 400 ml. of NaOH solution in the first scrubber (Fig. 35-13) and the same amount of  $\text{H}_2\text{O}_2$  (30%) in the second scrubber. This is the purification train for the combustion air.

When the apparatus is first assembled, adjust the valve between the vacuum manifold and the spray trap so that approximately 3 l. of air per minute will be drawn through the absorber when the chimney outlet is open to the atmosphere, the absorber is charged with  $30 \pm 2$  ml. of water, and the pressure in the vacuum manifold is maintained at approximately 40 cm. of water below atmospheric. When all adjustments have been made, remove the water from the absorbers.

With the burner control valve closed, the valve to the vacuum regulator fully open, and the pressure in the vacuum manifold adjusted to approximately 40 cm. of water below atmospheric, turn on the purified air. Adjust the chimney manifold control valve so that, at the required flow through the absorber, only a small stream of air escapes at the pressure-relief valve, a small stream of air enters at the vacuum regulator, and the pressure in the chimney manifold is 1 to 2 cm. of water.

When first assembling the apparatus, connect the gas sample line by means of glass or aluminum tubing to the inlet of the flowmeter. Connect the outlet of the flowmeter in a similar way to the lower side arm of the burner. Adjust the valve for controlling the rate of flow of gas so that gas is burned at a rate to liberate approximately 250 to 500 Btu per hour. This rate should be indicated by two index marks on the columns of the flowmeter. Make the primary air connection from the purified air line to the upper side arm of the burner by means of rubber or plastic tubing.

Wash the spray trap, absorber, and chimney well with water before each test. Charge the larger bulb of the absorber with 10 ml. of  $\text{Na}_2\text{CO}_3$  solution<sup>54</sup> and 20 ml. of water. Attach the spray trap and chimney, and connect them respectively to the vacuum line and to the purified air line by means of rubber or plastic tubing. Close the chimney opening by means of a cork.

*Procedure.*—Before the beginning of each test, purge the flowmeter, burner, and connection with the gas sample, and light the flame on the burner. Adjust the

<sup>53</sup> Tetrahydroxyquinone Indicator (THQ) is obtainable from the Betz Laboratories, Inc., Gillingham and Worth Sts., Philadelphia 24, Pa.

<sup>54</sup> This quantity of  $\text{Na}_2\text{CO}_3$  solution is adequate to absorb the  $\text{SO}_2$  from the combustion products of 1 cu. ft. of gas containing 15 grains of sulfur per 100 cu. ft. For higher concentrations of sulfur in the gas, the volume of  $\text{Na}_2\text{CO}_3$  solution should be proportionately increased, but the total initial liquid volume in the absorber should not exceed 30 ml.

the washings to the solution in the absorber. Add three drops of methyl orange indicator to the solution. Titrate the excess  $\text{Na}_2\text{CO}_3$  in the absorber with  $\text{HCl}$  to the methyl orange end point, mixing the solution after each addition of acid by alternate sucking and blowing on one end of the absorber.

Discharge the tan color of the acid methyl orange with a few drops of  $\text{Na}_2\text{CO}_3$  solution, and add 50 ml. of ethyl or isopropyl alcohol. Add about 0.5 g. of tetrahydroxyquinone indicator (THQ). After mixing the solution well, titrate with  $\text{BaCl}_2$  solution. After 1 or 2 ml. of the  $\text{BaCl}_2$  solution have been added, add 1 ml. of 0.1 N  $\text{AgNO}_3$  solution to intensify the rose color at the end point, and continue titration to the end point. The end point is reached when the color of the solution changes from yellow to rose, which is persistent with good mixing. Note and record the volume of  $\text{BaCl}_2$  solution required to produce the red color.

**Calculation of Results.**—Calculate the concentration of sulfur in grains per 100 standard cubic feet of gas from the results of the  $\text{BaCl}_2$  titration, as follows:

$$\text{Sulfur concentration} = \frac{A - 0.2}{V} \times 1.543,$$

where  $A$  = milliliters of  $\text{BaCl}_2$  solution required for the titration,

$V$  = volume of sample burned, in standard cubic feet, and

0.2 = blank subtracted from the  $\text{BaCl}_2$  titer to allow for the titration end point.

**Precision and Accuracy.**—The accuracy of the results of the determination depends on the accuracy with which the sample volume is metered as well as on the accuracy of the titration procedure. With care, when 1 cu. ft. of gas is burned, an absolute precision equivalent to  $\pm 0.1$  grain of sulfur per 100 cu. ft. of gas should be attainable in the  $\text{BaCl}_2$  titration, independent of the total quantity of sulfate present in the absorber. The over-all accuracy should therefore be between  $\pm 0.1$  and  $\pm 0.7$  grain of sulfur per 100 cu. ft., if metering accuracy of the  $\pm 2\%$  is attained, over the concentration range to which the procedure is adaptable.

The general procedure in ASTM Tentative Standard D1266-59T is similar to that just described, except that a mixture of 30% oxygen and 70% carbon dioxide is used for combustion in place of air; hydrogen peroxide solution is used as absorbent for the oxides of sulfur; and subsequent treatment is by titration with standard alkali. The use of the oxygen-carbon dioxide mixture prevents the formation of oxides of nitrogen during combustion of the sample. These acidic constituents would be absorbed in the absorbent and titrated as sulfur oxides. Barium chloride titration in D1072-56 precludes this error.

With either method the sulfur oxides can be determined gravimetrically by precipitation as barium sulfate.

### OTHER METHODS

For special applications other methods for determining organic or total sulfur may be applicable. For example, Lusby<sup>56</sup> devised a procedure, useful with gases containing hydrogen such as carburetted water gas or coke-oven gas, in which organic sulfur compounds are reduced to  $\text{H}_2\text{S}$  when the gas is passed over a heated platinum wire spiral. The hydrogen sulfide is then determined with a Tutweiler buret.

Shaw<sup>57</sup> describes a method by which hydrogen sulfide and mercaptans can be

<sup>56</sup> Lusby, O. W., American Gas Association Proceedings, 1936, p. 752.

<sup>57</sup> Shaw, J. A., Ind. Eng. Chem., Anal. Ed., 8, 162, 1936.

determined after absorbing them in a cadmium chloride solution using a special absorption bottle. Precipitated cadmium sulfide or mercaptide is determined by decomposing with acid iodine solution and back titrating with thiosulfate. The method is applicable to gases from any source or of any composition.

Hakewill and Rueck<sup>55</sup> proposed a procedure for the determination of several types of organic sulfur compounds. It makes use of selective absorbents in sequence to remove different sulfur compounds.  $H_2S$ , COS,  $CS_2$ , mercaptans, thiophenes are distinguished and determined by this procedure.

### WATER VAPOR

The concentration of water vapor in natural gas assumes considerable importance in high pressure transmission of that material, and in the operation of dehumidifying equipment. At temperatures prevailing in transmission lines hydrates of saturated hydrocarbon gases may be formed if water vapor is present. Deposits of the solid hydrates can impede the flow of gas, and are especially detrimental when formed in control equipment such as valves and regulators. On the other hand in some utility distribution systems, the gas at low pressure is deliberately rehumidified in order to protect the system from internal dust and to prevent drying out of some consumers' meters.

### DIRECT GRAVIMETRIC DETERMINATION

A basic method, adaptable to a wide range of concentrations, consists of passing a metered sample of gas through a desiccant such as calcium chloride, or "Deshydrite." Silica gel and activated alumina are unsuitable because they will absorb hydrocarbons. It is not advisable to use perchlorate desiccants in the presence of combustible gases.

The apparatus consists of three glass desiccant tubes such as U tubes connected in series, followed by a test meter. Gas is admitted to the drying train at substantially atmospheric pressure. One or more stages of pressure reduction will be required between a high pressure gas supply and the glass tubes. If the presence of entrained water droplets in the sample is suspected preheating with a sample line heater to vaporize the droplets may be required.

After filling the desiccant tubes and connecting them in series the air within the train is purged with gas under test. After suitable purging and after adjusting the pressure within them to atmospheric, the first two tubes are weighed on an analytical balance. Upon reconnecting them and recording the initial meter reading, gas is passed through the tubes at a slow rate. Meter temperature and the barometric pressure are recorded. At the end of the test period, determined by the rate of gas flow and the estimated moisture content, the tubes are again disconnected, adjusted to atmospheric pressure, and again weighed. The meter reading, temperature, and barometric pressure at the end of the test are recorded.

The concentration of water vapor in the sample is obtained by the expression

$$C_w = \frac{1543W}{V},$$

where  $C_w$  = the concentration of water vapor, grains per 100 cu. ft. of dry gas,

$W$  = the total gain in weight of the two drying tubes, grams,

$V$  = the sample volume, cubic feet at standard temperature and pressure, dry

<sup>55</sup> Hakewill, H., and Rueck, E. M., American Gas Association Proceedings 1946 p. 529

The concentration can be converted to other units, such as per cent by volume, relative humidity, or dew point with the aid of psychrometric tables.

#### DEW-POINT METHOD

The dew-point temperature of a gaseous fuel is the temperature at which the gas is saturated with water vapor at the existing pressure. Therefore, the partial pressure of water vapor in the gas sample is the saturation vapor pressure of water at the measured dew point.

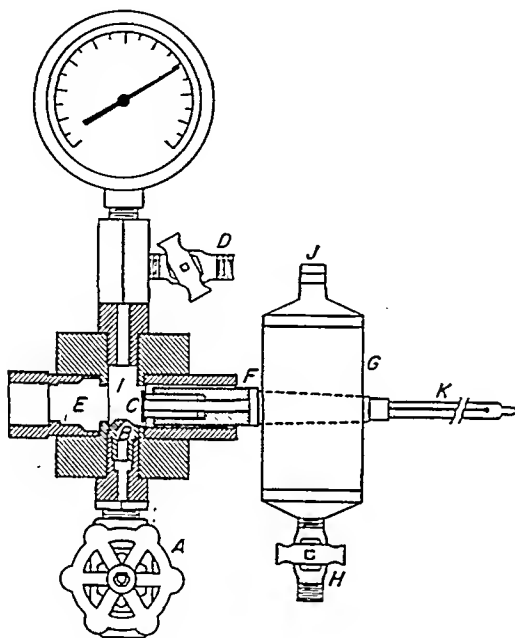


FIG. 35-14. Bureau of Mines Dew-Point Apparatus. (Reproduced with permission from ASTM Standards, ASTM, Philadelphia, 1958.)

ASTM Standard Method D1142-58<sup>59</sup> describes the determination of the water vapor content of gaseous fuels by measurement of the dew-point temperature. The Bureau of Mines dew-point apparatus, Fig. 35-14, is recommended, although any properly constructed dew-point apparatus meeting the following requirements may be used.

Means must be provided: (1) to permit a controlled flow of gas to enter and leave the apparatus while the apparatus is at a temperature at least 3°F. above the dew point of the gas; (2) to cool and to control the cooling rate of a portion (preferably a small portion) of the apparatus with which the *flowing* gas comes in contact to a temperature low enough to cause water vapor to condense from the gas; (3) to observe the deposition of dew on the cold portion of the apparatus; (4) to measure the temperature of the cold portion of the apparatus on which the dew

<sup>59</sup> Standard Method of Test for Water Vapor Content of Gaseous Fuels by Measurement of Dew-Point Temperature, D1142-58, ASTM Standards, Part 8, p. 1235, American Society for Testing and Materials, Philadelphia, Pa., 1958.

stream. Instruments are available using this principle,<sup>62</sup> with multiple "sensor" heads to cover a wide range of humidity conditions. Deaton<sup>63,64</sup> described a recording instrument of this kind, developed by the U. S. Bureau of Mines, which has been used to monitor continuously the water vapor concentration in high-pressure transmission lines.

Operating in a similar manner, a water vapor detector developed by Weaver<sup>65</sup> uses a film of a mixture of sulfuric and phosphoric acids on the surface of an insulator between two platinum electrodes. The electrical conductance of the film is an indication of the humidity of the gas to which it is exposed.

## NITROGEN COMPOUNDS

In coke oven and manufactured gas practice it is at times necessary to determine the concentration of ammonia, cyanogen or hydrocyanic acid, and certain nitrogen oxides which occur in these gases in small quantities.

### AMMONIA

Ammonia is absorbed from a metered volume of gas in standard acid solution and the resulting solution titrated directly with alkali.<sup>66</sup>

*Apparatus.*—Two gas wash bottles are connected in series, and the outlet of the train connected to the inlet of a 0.1 cu. ft. wet test meter.

*Reagents.* Standard Acid.—Add 1.25 to 1.5 ml. concentrated sulfuric acid to distilled water and make up to 2 l. in a volumetric flask. Standardize by precipitation of sulfate as BaSO<sub>4</sub>.

Standard Alkali.—Dissolve 1.8 g. of sodium hydroxide in distilled water; make up to 2 l. in a volumetric flask. Stir until completely dissolved and well mixed. Standardize by comparing with the standard acid, using methyl orange indicator.<sup>67</sup>

*Procedure.*—By means of a buret, measure 25.0 ml. of the standard acid into each of two gas scrubbing bottles; add a few drops of indicator; add enough water to obtain good scrubbing; connect the bottles and meter in series as described and connect the inlet of the train to the gas supply. Record the meter reading. Pass gas through the train at a rate of 0.5 to 0.6 cu. ft. per hour for 2 to 5 hours; turn off the gas and again record the meter reading. Transfer the solutions to a 400-ml. beaker and titrate with standard acid or alkali until the end point is reached. The ammonia concentration in the gas is calculated by the expression

$$X = \frac{(a - b)(0.0170)(15.43)(100)}{C},$$

where  $X$  = grains ammonia per hundred cubic feet of gas at 60°F., 30 in. Hg, saturated,

$a$  = milliequivalents of standard acid taken,

$b$  = milliequivalents of standard alkali used, and

$C$  = cubic feet of gas passed, corrected to 60°F., 30 in. Hg, saturated

<sup>62</sup> American Instrument Co., Silver Springs, Md.

<sup>63</sup> Deaton, W. M., American Gas Association Proceedings, p. 1062, 1953.

<sup>64</sup> Deaton, W. M., and Frost, E. M., Jr., U. S. Bureau of Mines, R.I. 3399, 1938.

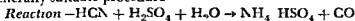
<sup>65</sup> Weaver, E. R., American Gas Association Proceedings, p. 476, 1956.

<sup>66</sup> N.B.S. Circular No. 48, Standard Methods of Gas Testing, 2nd ed., 1916.

<sup>67</sup> Sodium alizarinsulfonate solution may be used in place of methyl orange. One gram sodium alizarinsulfonate is dissolved in 100 ml. water, and the solution filtered. The color changes from greenish-yellow to light brown at the end point. Red is produced beyond the end point.

## CYANOGEN AND HYDROGEN CYANIDE

These components are usually determined together because of the similarity of their chemical reactions and reported as HCN. Many methods of determination have been described to meet special conditions. However the following is a generally suitable procedure.



**Procedure**—Assemble gas purifying train so as to pass a stream of gas through 3 gas washing bottles or test tubes and a meter. Place 25 ml of 10%  $\text{H}_2\text{SO}_4$  solution in bottle No 1 to remove free  $\text{NH}_3$ . In each of the other two bottles, place 25 ml of concentrated  $\text{H}_2\text{SO}_4$ . Purge sample line and pass representative stream of gas at rate of about 1 cu ft per hour until measurable amount of HCN is absorbed then disconnect train. Observing safe practices transfer concentrated acid from last two bottles to a 1 liter Kjeldahl flask containing about 250 ml of water. Rinse bottles and add washings to flask. Install flask in ammonia distillation apparatus add excess of strong sodium hydroxide solution distill and collect the ammonia in measured excess of 0.1 N  $\text{H}_2\text{SO}_4$ . Titrate with 0.1 N NaOH using methyl red as indicator. HCN content of gas is obtained from test data by expression

$$G = A(0.0027)(15.43)(100)/V$$

$$= \frac{4.17A}{V}$$

where  $G$  = grains HCN per 100 cu ft of gas,

$A$  = milliliters of standard acid consumed,

0.0027 = grams of HCN per milliliter of 0.1 N standard acid consumed

$V$  = volume of gas sample cubic feet at 60°F, 30 in Hg saturated

This procedure is not recommended for carburetted water gas since concentrated sulfuric acid reacts with unsaturated hydrocarbons present. It is applicable to blue gas. However Seil<sup>68</sup> states that this is the simplest and most accurate of all standard methods. All HCN and  $(\text{CN})_2$  are hydrolyzed to ammonia whereas in methods depending on alkaline absorption all the HCN but only half the  $(\text{CN})_2$  absorbed can enter into the reactions on which the methods are based. Thus higher results are usually obtained with the acid method than in others.

## OXIDES OF NITROGEN

Both nitric oxide NO and nitrogen dioxide  $\text{NO}_2$  have been found in minute concentrations in coke oven gas and in carburetted water gas. They are also formed in combustion products and may assume some importance in atmospheric pollution. In fuel gas purification practice it is not sufficient to remove the NO since the presence of oxygen even in small concentrations will slowly convert the NO present to nitrogen dioxide. The latter reacts with unsaturated hydrocarbons to form gummy deposits in critical parts of consumers appliances and may cause malfunctioning.

A number of analytical methods for determining NO have been proposed. In all of them NO is oxidized to  $\text{NO}_2$  which is subsequently determined colorimetrically. Air or oxygen hydrogen peroxide chromic acid or potassium permanganate have been used as oxidizing agent. Either Griess reagent or *m*-phenylenediamine

<sup>68</sup> Seil G. E. Dry Box Purification of Gas American Gas Association N Y 1943



is used for colorimetric determination. A shortcoming of all methods, however, seems to be incomplete conversion of NO or incomplete recovery of NO<sub>2</sub> formed. Even though calibration of the selected procedure would be required for correct results, comparative results without correction have usually been satisfactory in practice.

Fulweiler<sup>69</sup> has described an apparatus and procedure which has been used primarily with carburetted water gas, or mixed gas distributed by utility companies, and seems to be the most reliable method. Nitric oxide present in the gas is

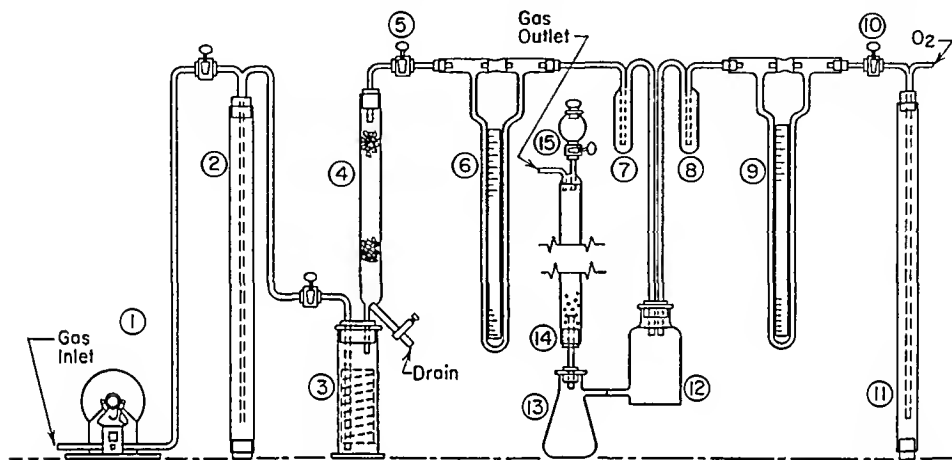


FIG. 35-15. Apparatus for Nitric Oxide Determination. (Reproduced with permission from AGA Proceedings, American Gas Assn., New York, 1933.)

oxidized to NO<sub>2</sub> by oxygen, which is mixed in equal parts with the gas containing the NO. There appears to be a catalytic effect by certain unsaturated components in the gas, and the conversion takes place with a reaction time much less than would be expected according to the normal reaction rate. Maximum recovery of NO<sub>2</sub> was experimentally determined to be obtained in about 2 minutes with most gases.

Griess-Ilosvay reagent is used as the absorbent and colorimetric solution in preference to *m*-phenylenediamine because of its greater sensitivity and stability. When properly prepared it is colorless, and may be kept in brown bottles for periods up to a year without deterioration.

#### Apparatus (Fig. 35-15).

1. Small, double piston, electrically driven gas pump used when gas pressure is irregular or not sufficient to overcome the back pressure of the apparatus.

2. Glass cylinder filled with water to function as a constant pressure-regulating device for gas.

3. Milligan gas washing bottle containing 1 to 1 KOH solution for removing H<sub>2</sub>S and other impurities. (Gases containing an appreciable quantity of ammonia vapor are washed with normal H<sub>2</sub>SO<sub>4</sub> in a bottle preceding the KOH solution.)

4. Cylindrical tube containing KOH pellets for further purification.

5. Glass stopcock for regulating flow of gas.

<sup>69</sup> Fulweiler, W. H., American Gas Association Proceedings, p. 829, 1933.

- 6 Gas flow meter
- 7 Trap to protect mixing bottle (outlet of gas flow meter)
- 8 Trap to protect mixing bottle (outlet of oxygen flow meter)
- 9 Oxygen flow meter
- 10 Glass stopcock for regulating flow of oxygen
- 11 Glass cylinder filled with water to function as a constant pressure regulating device for oxygen
- 12 One half liter reaction bottle for mixture of oxygen and gas
- 13 250 ml Erlenmeyer flask for receiving washings of absorption tower
- 14 Absorption tower filled with 4 mm glass beads
- 15 Separatory funnel for adding small increments of Griess reagent during test.

It is necessary that the apparatus should be kept very clean at all times and that at least once a week the reaction bottle and the absorbing tube and beads should be thoroughly cleaned with chromic acid cleaning mixture washed with distilled water and dried in an oven preferably an electric oven. On the first test after cleaning the apparatus should be allowed to purge for one half hour.

**Reagents** Griess Reagent—Dilute 250 ml cp glacial acetic acid to 1 liter with nitrite free water.<sup>70</sup> Dissolve 2.0 g of cp sulphanilic acid in 600 ml of this solution. Solution is accelerated by heating the dilute acid.

Add 0.4 g of alpha naphthylamine to 200 ml of hot distilled water. Cool and filter into 400 ml of the dilute acetic acid. When both solutions have cooled mix and keep in brown glass stoppered bottles.

**Standard Nitrite Solution**—Dissolve 0.115 g  $\text{NaNO}_2$  in 1 liter of nitrite free distilled water. After thorough mixing pipet 10 ml of this solution into a 1 liter volumetric flask and dilute to 1 liter with distilled water. One ml standard  $\text{NaNO}_2$  solution =  $1 \times 10^{-6}$  g NO.

**Procedure**—Purge the apparatus for one hour before making a quantitative test. This must be done especially after renewing the KOH purifying solution or pellets. Gas and oxygen flow are each adjusted to equal rates of 0.4 cu ft per hour as indicated by the flowmeters. As the test progresses add Griess reagent from the separatory funnel to the absorption tower in increments of about 10 ml each 10 minutes. At the conclusion of the test shut off gas and oxygen flow. Wash the absorber with small portions of Griess reagent until it appears colorless. Disconnect the Erlenmeyer flask and transfer the red colored solution to a Nessler or colorimeter tube. Make volume up to the mark with Griess reagent. With Nessler tubes compare the color with a series of known standards made up from standard sodium nitrite solution and Griess reagent. If a colorimeter is used compare the absorbance of the unknown solution with that of a known standard of nearly the same color.

**Calculation**—The concentration of NO in the gas is then calculated by the expression

$$\text{NO (g per } 10^6 \text{ cu ft)} = \frac{M}{V} \times 10^{-6}$$

where  $M$  = number of milliliters of standard nitrite solution giving same color intensity as unknown,

$V$  = volume of gas passed during test, cubic feet

<sup>70</sup> It is necessary to observe great care with the purity of the reagents used especially the distilled water. All reagents should be tested for the presence of oxides of nitrogen.

It was determined experimentally that the recovery of the nitric oxide varies somewhat with the concentration in the gas. To obtain a more nearly correct value, the following correction factors reported by Fulweiler<sup>69</sup> may be used.

## CORRECTION FACTORS FOR NO DETERMINATION

<i>Observed Concentration</i> NO (g. per 10 <sup>6</sup> cu. ft.)	<i>Correction</i> <i>Factor</i>
100	2.68
75	2.87
50	3.06
25	3.25
10	3.37

However, for comparative purposes, using the same apparatus and procedure, the observed values are often sufficient for control purposes.

Shaw's<sup>71</sup> modification of the Schuftan<sup>72</sup> method is similar, except that a longer reaction time is provided. He has used his method only with coke-oven gas. Observed concentrations by the two methods cannot be compared because correction factors differ. The Fulweiler method has been applied to coke-oven gas, and is presumably adaptable to any manufactured gas. The necessary modification consists of adding butadiene to the reacting mixture of gas and oxygen at a concentration of about 1% by volume in the mixture. The addition is made directly to the stream entering the reaction bottle.

Hollings<sup>73</sup> describes the Guyer and Weber method<sup>74</sup> in which NO is oxidized by acidified potassium permanganate solution. Again, correction factors must be determined experimentally, and observed results cannot be compared with those obtained by other methods. Another difficulty encountered with this procedure is reaction of the permanganate with certain constituents of the gas, destroying the reagent.

## CARBON MONOXIDE

Toxic quantities of carbon monoxide, CO, from combustion products of almost any combustible material, may enter the atmosphere and be a serious hazard in many localized situations. The concentrations of concern in this respect are less than 0.1% by volume, and in most cases are far below the limit of detection by volumetric absorption procedures described earlier. Instruments and methods of detection for purposes considered here must be capable of reliable analysis to hundredths or thousandths of one per cent.

TOXICITY AND HAZARDS OF CARBON MONOXIDE<sup>75, 76</sup>

Carbon monoxide is an odorless gas. Although it may be at times associated, in products of incomplete combustion, with odorous products such as aldehydes

<sup>71</sup> Shaw, J. A., *Ind. Eng. Chem., Anal. Ed.*, 8, 162, 1936.

<sup>72</sup> Schuftan, P., *Brennstoff-Chemie*, 13, 104, 1932.

<sup>73</sup> Hollings, H., *Communication No. 147*, Institution of Gas Engineers, London, 1936.

<sup>74</sup> Guyer, A., and Weber, R., *Brennstoff-Chemie*, 14, 405, 1933.

<sup>75</sup> Hamilton, A., and Hardy, H. L., *Industrial Toxicology*, 2nd ed., Paul B. Hoeber, Inc., N. Y., 1949.

<sup>76</sup> Henderson, Y., and Haggard, W. H., *Noxious Gases and the Principles of Respiration Influencing Their Action*, 2nd ed., Reinhold Publishing Corp., N. Y., 1943.

and alcohols the absence of odor gives no assurance that trace quantities of CO are not present

Carbon monoxide is an asphyxiant entering the body by respiration. In the blood stream it combines with hemoglobin driving oxygen out and thereby depriving the body of its normal oxygen supply. The affinity of hemoglobin for CO is many times as great as its affinity for oxygen and the product of reaction is more stable. The quantity of CO absorbed in the blood of a person exposed to it and consequently the physiological effect depends on its concentration in air, duration of exposure, physical condition and activity of the person when exposed. Table 35-8 illustrates the effect on an average person of breathing air containing small percentages of CO.

TABLE 35-8<sup>76</sup> PHYSIOLOGICAL EFFECTS OF SMALL CONCENTRATIONS OF CO IN AIR

<i>CO Concentration</i>		
<i>p p m</i>	<i>Per Cent</i>	<i>Effect</i>
100	01	Allowable concentration for several hours exposure
400-500	0.04-0.05	May be inhaled for one hour without appreciable effect
600-700	0.06-0.07	Causes just appreciable effect (headache) after one hour exposure
1000-1200	0.10-0.12	Unpleasant but not dangerous symptoms after one hour exposure
4000 and over	0.40 and over	Fatal with less than one hour exposure

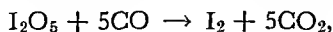
Table 35-9 indicates symptoms of carbon monoxide exposure

TABLE 35-9<sup>76</sup> SYMPTOMS OF CARBON MONOXIDE EXPOSURE

<i>Percentage of CO in Air</i>	<i>Effects</i>
0.02	Possibly headache, mild frontal in 2-3 hours
0.04	Headache, frontal and nausea after 1-2 hours, occipital after $2\frac{1}{2}$ - $3\frac{1}{2}$ hours
0.08	Headache, dizziness, and nausea in $\frac{3}{4}$ hour, collapse and possibly unconsciousness in 2 hours
0.16	Headache, dizziness, and nausea in 20 minutes, collapse unconsciousness, possibly death in 2 hours
0.32	Headache and dizziness in 5-10 minutes, unconsciousness and danger of death in 30 minutes
0.64	Headache and dizziness in 1-2 minutes, unconsciousness and danger of death in 10-15 minutes
1.28	Immediate effect unconsciousness and danger of death in 1-3 minutes

IODIMETRIC (IODINE PENTOXIDE) METHOD <sup>77, 78, 79, 80</sup>

Iodine pentoxide oxidizes CO according to the equation



liberating iodine stoichiometrically which is absorbed in KI solution and titrated with standard sodium thiosulfate with starch indicator. Using a known sample volume, the concentration of CO present can be calculated. In determining the concentration of CO in combustion products of certain gas-burning appliances, the sample, not taken directly from a flue, is frequently diluted with air in the

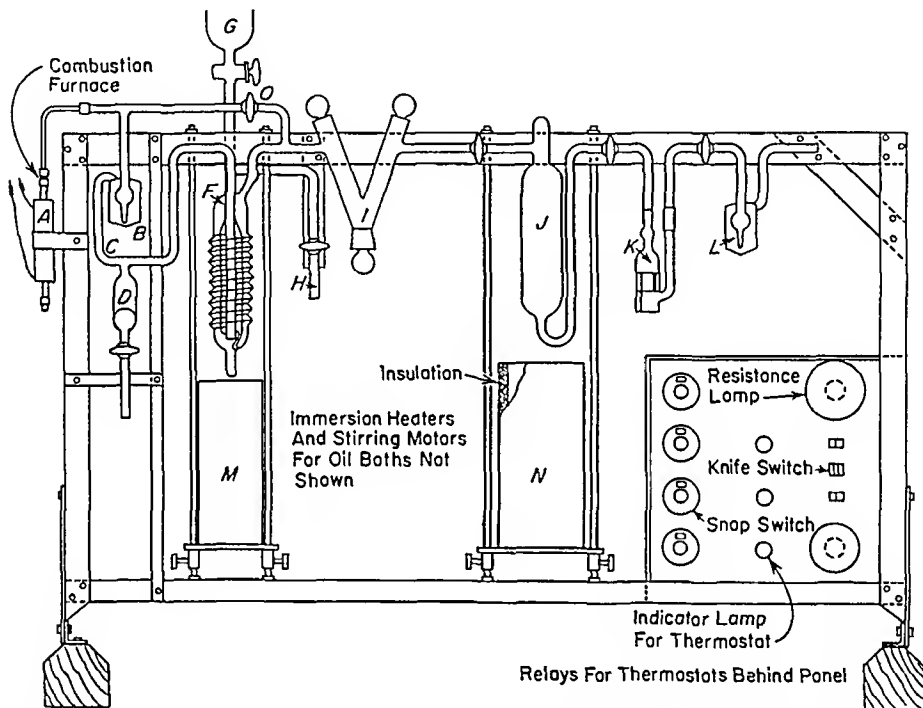


FIG. 35-16. Iodine Pentoxide Apparatus, Bureau of Standards Modifications. (Reproduced with permission from American Gas Assn., New York, 1933.)

process of collection. The concentration in the combustion products alone, on an air-free basis, may be desired. The usual procedure is to determine the free oxygen in the sample, and convert the analytical results to an air-free basis. It can also be accomplished by determining  $\text{CO}_2$  in the sample, if the concentration of  $\text{CO}_2$  in stoichiometric combustion products is known.

**Apparatus.**—Figure 35-16 represents one form of apparatus used for the iodimetric determination of CO.<sup>77</sup> A resistance furnace, *A*, heats a porcelain tube

<sup>77</sup> Gas Chemists' Handbook, 3rd ed., American Gas Association, N. Y., 1929.

<sup>78</sup> Teague, M. C., Ind. Eng. Chem., 12, 964, 1920.

<sup>79</sup> Vandaveer, F. E., and Gregg, R. C., American Gas Association Monthly, p. 469, August, 1929.

<sup>80</sup> Vandaveer, F. E., Gas, 5, 18, p. 24, October, 1942.

filled with palladium asbestos to 700–750°C through which purge gas enters the apparatus. *B* and *C* form a mercury sealed trap. The sample enters through the float valve *D* and *E* which is shut off by the sample confining water when all of the sample has entered the apparatus. A Greiner-Friedrichs type scrubber *F* is shown although glass bead towers have also been used. This vessel contains a concentrated sulfuric acid-potassium dichromate mixture to oxidize all combustible constituents other than CO which may be present in the sample. There follows a P<sub>2</sub>O<sub>5</sub> drying tube *I* and the cylindrical bulb *J* containing iodine pentoxide supported on glass wool. The Gomberg absorption bulb *K* containing KI solution and a second mercury trap *L* complete the train. The acid dichromate solution is heated to 100°C by oil bath *M*. The I<sub>2</sub>O<sub>5</sub> container is heated to 150°C by the oil bath or thermostated electric heater *N*.

**Reagents** Chromic Acid—Concentrated c.p. sulfuric acid saturated with potassium dichromate.

**Iodine Pentoxide** I<sub>2</sub>O<sub>5</sub>—The reaction bulb is filled with high purity I<sub>2</sub>O<sub>5</sub> separated and dispersed with glass wool to prevent channeling. It is conditioned and stabilized by purging two days at about 210°C with air or nitrogen followed by another two days at 150°C. Prior to use some KI solution in the Gomberg absorber should show no trace of iodine after 2 or 3 hours purging when starch is added. After this conditioning the I<sub>2</sub>O<sub>5</sub> may be used daily up to a year with samples of reasonably small CO concentrations.<sup>9, 10</sup>

**Potassium Iodide**—A solution 10% by weight of KI in distilled water. Fresh solution should show no trace of free iodine.

**Sodium Thiosulfate**—Approximately 0.001 normal solution is required containing 0.2482 g Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> · 5H<sub>2</sub>O per liter. Allow to stabilize several weeks before standardizing against resublimed iodine. Check the normality periodically.

**Starch Indicator**—Dissolve 1 g soluble starch in a little water. Add to 250 ml of boiling water, stir, cool and decant clear starch solution.

**Procedure**—Purge the train thoroughly with CO-free nitrogen. Connect sample bulb to inlet so that it enters train through *D*. Sample bulb is immersed in water in a suitable container. Connect suction to outlet of train. Open stopcocks of sample bulb and stopcock of inlet to apparatus. Adjust suction by observing bubbling in the Gomberg absorber. Continue purge while part of sample is drawn through *L*, then shut off. When the sample is completely drawn into apparatus water will cause float valve *E* to close. At this point resume purge gas flow.

All combustibles other than CO are oxidized to CO<sub>2</sub> by the chromic acid. The gas stream is dried by the P<sub>2</sub>O<sub>5</sub>. CO is oxidized by I<sub>2</sub>O<sub>5</sub> and liberated iodine is carried by the gas stream into the KI solution where it is absorbed. Continue purge until all liberated iodine has been recovered which may take from one-half hour to an hour depending on the CO concentration.

At the end of the test period transfer the absorbent solution from the Gomberg bottle to an Erlenmeyer flask. Wash the Gomberg bottle with distilled water and add washings to the flask. Titrate with standard thiosulfate solution to the disappearance of blue color formed when starch solution is added.

**Calculation**—

$$1 \text{ ml of } 0.001 \text{ Na}_2\text{S}_2\text{O}_3 = 0.0558 \text{ ml of CO (0°C, 760 mm)}$$

$$\text{per cent CO in sample} = \frac{\text{ml of Na}_2\text{S}_2\text{O}_3 \times 0.0558 \times 100}{\text{volume of sample (ml at 0°C, 760 mm)}}$$

## COLORIMETRIC METHOD

A simple and rapid colorimetric test, highly useful in field or laboratory, has been developed by Shepherd and co-workers<sup>81</sup> at the National Bureau of Standards. It is capable of detecting and determining less than 1 part of carbon monoxide in  $5 \times 10^8$  parts of air in 20 minutes; of detecting as little as 0.001% by volume in one minute; or of determining physiologically significant amounts (0.01 to 0.4%) in about a minute. Kits are now available<sup>82</sup> containing all necessary equipment, including sealed tubes of reagent ready to use. Shepherd says the indicator is silica gel impregnated with ammonium molybdate, sulfuric acid, and palladium sulfate. A yellow silicomolybdate complex is formed, which is reduced by CO when catalytically influenced by palladium. The yellow color changes to shades of greenish blue when reduced, indicating the carbon monoxide concentration.

*Procedure.*—A laboratory procedure is described<sup>81</sup> in which air to be tested is passed through a tube of indicator at 90 ml. per minute for a definite period. The color developed is compared with freshly prepared standards which are similar indicator tubes exposed to known amounts of carbon monoxide. In the range 0 to 0.01% by volume, CO can be determined by this means with a reproducibility of 0.0002% and probable accuracy of 0.001% or better.

However, the field method, as represented by available kits, is probably the far more widely used. A 2-ounce aspirator bulb, equipped with a rate-controlling device, is attached to one end of a prepared indicator tube immediately after breaking off the tips of the glass tube. Air is drawn through the indicator with one or more squeezes of the bulb. The resulting color of the indicator is compared with a color chart supplied with the instrument, from which the CO concentration is read. With multiple squeezes a concentration as low as 0.001% can be measured. A maximum reading represents about 0.1% CO.

*THE HOOLAMITE IODINE-PENTOXIDE INDICATOR* (Fig. 35-16)<sup>83, 84</sup>

The Hoolamite indicator<sup>85</sup> is a small hand-operated device for detecting and estimating carbon monoxide in atmospheres often encountered around furnaces, in mines, or other confined places. It will show concentrations of 0.07% or more. The apparatus is simple, and no skill is required; anyone can make a test in about a minute.

The indicator consists of a tube of activated charcoal through which the gas is drawn by means of a rubber hand bulb; this discharges through a small glass tube containing the Hoolamite, a white or light gray granular substance composed of iodine pentoxide and fuming sulfuric acid on pumice granules. Interfering gases, if not present in large amounts, are removed by the charcoal; interfering dusts and mists are removed by cotton wool filters placed after the charcoal tube.

At ordinary temperatures carbon monoxide is oxidized by the Hoolamite, and iodine is liberated. The granules become colored through increasing shades of bluish green, then brownish purple, or black, according to the concentration of the carbon monoxide. A comparison of the shade of blue-green produced with a permanent color scale placed beside the active tube enables one to estimate the

<sup>81</sup> Shepherd, M., *Anal. Chem.*, 19, 77, 1947.

<sup>82</sup> Mines Safety Appliances Co., Pittsburgh, Pa., United States Safety Service Co., Kansas City, Mo.

<sup>83</sup> Hoover, C. R., *Ind. Eng. Chem.*, 13, 770, 1921.

<sup>84</sup> Katz, S. H., and Bloomfield, J. J., *Ind. Eng. Chem.*, 14, 304, 1922.

<sup>85</sup> Mines Safety Appliances Co., Pittsburgh, Pa.

concentration of the carbon monoxide from a lower limit of 0.07% to 1% or more. The small glass tubes of Hoolamite are tapered at the ends and sealed against moisture which causes deterioration. The tips are broken open and the tube inserted in place immediately before making a test.

### INSTRUMENTS

There are a number of instruments available on the market for the determination of carbon monoxide in air at the low concentrations of concern. Portable indicating as well as recording models are produced. Their reliability is high.

**MSA Carbon Monoxide Indicator**<sup>86</sup>—By means of a small pump a sample of air is drawn at fixed rate through a flowmeter and desiccant canister into a catalyst chamber where CO is oxidized to  $O_2$ . In the presence of the catalyst Hopcalite the reaction takes place at room temperature. Heat is released in proportion to the quantity of CO oxidized resulting in a temperature rise in the catalyst bed. A series of thermocouples embedded in the catalyst register the temperature rise on a millivoltmeter calibrated to read directly in per cent CO. The scale range is from 0 to 0.15% with divisions of 0.005%.

A recording instrument based on the same operating principle is manufactured<sup>86</sup> and has found wide use. One of its earliest applications was for monitoring the carbon monoxide in vehicular tunnels.

**LIRA**<sup>8</sup> *Carbon Monoxide Recorder*—The absorption of infrared radiation by carbon monoxide is used to produce an indication and record of CO in concentrations of 0 to 0.1% with little instrumental delay.

In operation beams of infrared radiation of equal intensity pass through two absorption cells. One cell contains CO free air, the other the sample to be analyzed. Any CO in the sample absorbs radiation from the beam passing through it in proportion to the concentration.

If the infrared beam which has passed through the blank cell is then passed through a detector cell containing air with a small fixed amount of CO, radiation absorbed will cause a temperature rise in the detector cell. The beam passing through the unknown sample will lose part of the energy which can be absorbed by CO. Then in the detector cell the energy deficient beam will cause less temperature rise than the beam which passed through the blank.

Ingenuous design provides for combining the two beams in the detector cell in such a way as to give a rapidly fluctuating temperature change. A corresponding sensor fluctuation is amplified and converted to a signal proportional to the concentration of CO in the gas sample.

The versatility of the LIRA instrument is attractive in that appropriate selection of the detector cell will permit its use for detecting molecular species other than CO. Very small concentrations of hydrocarbons in air can be detected.

<sup>86</sup> Mines Safety Appliances Co. Pittsburgh, Pa.

<sup>8</sup> LIRA stands for Luft Type Infra Red Analyser.



## Chapter 36

# GAS ANALYSIS— VACUUM TECHNIQUES

By W. G. Guldner

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**Introduction.**—The presence of oxygen, hydrogen, nitrogen, and carbon in metals and alloys has been found, in many instances, to produce detrimental effects on the physical and electrical properties of these metals and alloys. The impurity level may vary greatly from a few parts per million to several thousand. In view of this, it has been necessary to devise special apparatus for collecting, measuring, and analyzing these impurities. As the amount of gas normally available for analysis is relatively small, i.e., below the amount required for Orsat analysis, vacuum techniques have been found to be most suitable.

The theoretical aspects relating to vacuum have been adequately covered by many scientists well qualified in their fields. Numerous texts have been published here and abroad covering many phases of vacuum technology and applied techniques. The purpose of this chapter is not to review such detailed discussions, but to describe some of the vacuum techniques that have been useful in making analytical measurements, and, secondarily, to recommend that the interested reader refer to the principles of vacuum in such outstanding works as Dushman<sup>1</sup> and Reimann.<sup>2</sup> References to the application of vacuum techniques to analytical chemistry appear regularly in *Chemical Abstracts* and *Transactions of the American Vacuum Society*.

Seldom will a specific design of apparatus fulfill all of the requirements of a laboratory, where accuracy, impurity range, time of analysis, and cost are governing factors. The following summary describes the principles used in good vacuum practice, involving the means for: collection, measurement, and analysis of micro gas samples; injection of metal samples into a vacuum station; admission of gas to an evacuated system; devices for removing gas from glass and metal enclosed units; and methods for the determination of oxygen, hydrogen, nitrogen, and carbon in metals.

Most metals contain carbon, oxygen, hydrogen, and nitrogen in either a free or combined state. When these metals are heated in vacuum, gas is evolved that may contain carbon monoxide, carbon dioxide, hydrogen, water vapor, and hydrocarbons; such inert gases as nitrogen, helium, and argon may also be present.

<sup>1</sup> Dushman, S., *Production and Measurement of High Vacuum*, General Electric Review, 1922; *Vacuum Technique*, John Wiley & Sons, New York, 1949.

<sup>2</sup> Reimann, A. L., *Vacuum Technique*, Chapman and Hall, Ltd., London, 1952.

These gases are measured at reduced pressure and in the unit of cc mm (1 cc. at 1 mm pressure) or micron liter. Both terminologies are used for the same unit. This unit is micro in dimensions as shown in Table 36.1

TABLE 36.1 WEIGHT EQUIVALENTS, 1 CC MM AT 25°C

<i>Gas Measured</i>	<i>Sought</i>	<i>Micrograms</i>
CO <sub>2</sub>	CO <sub>2</sub>	2.37
	C	0.65
	O <sub>2</sub>	1.72
CO	CO	1.51
	C	0.65
	O <sub>2</sub>	0.86
H <sub>2</sub> O	H <sub>2</sub> O	0.97
	H <sub>2</sub>	0.11
	O <sub>2</sub>	0.86
O <sub>2</sub>	O <sub>2</sub>	1.72
H <sub>2</sub>	H <sub>2</sub>	0.11
N <sub>2</sub>	N <sub>2</sub>	1.51

## COLLECTION, MEASUREMENT, AND ANALYSIS OF MICRO GAS SAMPLES

The most acceptable method for quantitatively measuring these gases excluding water is by means of a McLeod gauge.<sup>3</sup> This is an absolute pressure gauge that can be easily designed to obtain maximum sensitivity and range for a given application. This gauge appears in several forms throughout this chapter and is used in linear and quadratic scale manner in the form of a capillary pipet where all the gas is confined in the bulb (see Vacuum Fusion Apparatus p 1580) and as a rotary Lippincott design of gauge.

A low pressure micro gas analytical apparatus was first described by Langmuir.<sup>4</sup> Additional modifications and improvements were made by Ryder,<sup>5</sup> Prescott,<sup>6</sup> Dalton,<sup>7</sup> Norton,<sup>8</sup> and others. A good example of such an apparatus is shown in Fig. 36.21 p 1581. In general the apparatus consists of a McLeod gauge for the measurement of pressure in a known volume. In this manner the quantity of gas pressure times volume (PV) is determined. A mercury diffusion pump and

<sup>3</sup> See Methods of Measurement p 1587 under Vacuum Fusion Apparatus also see Fig. 36.28

<sup>4</sup> Langmuir I. J. Amer. Chem. Soc. **34**, 1310 1912

<sup>5</sup> Ryder H. M. J. Amer. Chem. Soc. **40**, 1656 1918

<sup>6</sup> Prescott C. H. Jr. J. Amer. Chem. Soc. **50**, 3237 1928 with Morrison J. Apparatus for Microanalysis of Gas Ind. Eng. Chem. Anal. Ed. **11**, 230 1939

<sup>7</sup> Dalton R. H. J. Amer. Chem. Soc. **57**, 2150 1935

<sup>8</sup> Norton F. J. and Marshall A. L. Trans. Am. Inst. Mining and Met. Engrs. **109**, 28 1932 104, 136 1933

Toepler pump are used to collect and circulate the gas over suitable reagents. In most cases where the amount of gas is small, mercury cutoffs are used in preference to stopcocks. Stopcocks with oblique bore, hollow plug, and special grinding are satisfactory, however, when the ground surfaces are lubricated lightly with a suitable grade of Apiezon vacuum grease. Several schemes for the analysis of gases at low pressure have been proposed. Most of these methods are based on the measurement of the PV relationship, followed by the separation of a component in the gas mixture by reaction or absorption of the gas by a reagent, by fractional freezing, or by a combination of the two. The resulting PV is subtracted from the former as a measure of the component. These are the methods that will be used in specific gas metal studies described hereafter.

The selection of the most suitable analytical method depends on the time required for analysis, precision, availability of the equipment, and the composition of the gas mixture. The most common methods employed for separation and measurement are by selective absorption on solid reagents, fractional freezing, fractional distillation, diffusion, see p 1593, mass spectrometry, thermal conductivity, and gas chromatography.

### SCHEME OF ANALYSIS

The micro gas methods described here involve the use of selective sorption and fractional freezing. The general scheme of analysis is shown in Table 36.2

In the final summary, the total hydrogen found by analysis must be corrected by the amount added in Step 6.

### SEPARATION OF GASES BY FRACTIONAL FREEZING

Rapid separations of gases at low pressures can be obtained through the use of liquid oxygen, liquid nitrogen, or dry ice. In some special cases, solvent mushes<sup>9</sup> are employed. The most common method for the separation of water vapor and carbon dioxide from other gases is as follows: (1) circulate the gas mixture through a liquid nitrogen trap to freeze out the carbon dioxide and water vapor, (2) collect noncondensable gas in a pipet, (3) transfer the gas frozen out in the liquid nitrogen trap to a closed end manometer by removing the liquid nitrogen from the trap and placing it about the end of the manometer. The carbon dioxide and water vapor are then recondensed in the end of the manometer.<sup>10</sup> The mercury is raised in the manometer and dry ice is substituted for the liquid nitrogen. The gas over the dry ice is carbon dioxide and the pressure is measured in millimeters of mercury and at a known volume. The carbon dioxide is removed to pump, or for further identification by absorption in Ascarite. Close manometer, and (4) remove the dry ice from the end of the manometer and allow the temperature to rise to ambient. Compress the water vapor to a known volume and measure the pressure. The pressure must be below the vapor pressure of water at room temperature to assure that the water is all in the gas phase.

These are the gases that are normally encountered in gas metal studies. In most instances, the mixture does not have more than 3 gases, thereby simplifying the analysis and reducing the time. The procedures described above are then used

<sup>9</sup> Sanderson, R. T. *Vacuum Manipulation of Volatile Compounds*, John Wiley & Sons, New York 51-5, 1948.

<sup>10</sup> Guldner, W. G., and Beach, A. L., *Gasometric Method for Determination of Hydrogen in Carbon*, Anal. Chem. 26, 1199, 1954.

TABLE 36-2 SEPARATION OF  $\text{H}_2\text{O}$ ,  $\text{CO}_2$ ,  $\text{CO}$ ,  $\text{H}_2$ ,  $\text{O}_2$ ,  $\text{N}_2$ , AND  $\text{CH}_4$ 1 Separation by Fractional Freezing  
Liquid Nitrogen

Condensable		Noncondensable
$\text{H}_2\text{O}$	$\text{CO}$	$\text{CO}$ , $\text{H}_2$ , $\text{O}_2$ , $\text{N}_2$ , $\text{CH}_4$
2 Transfer from trap to closed-end manometer * with liquid nitrogen, raise mercury column and replace nitrogen with dry ice, noncondensable— $\text{CO}_2$ Measure PV		5 $\text{CO}$ , $\text{H}_2$ , $\text{O}_2$ , $\text{N}_2$ , $\text{CH}_4$ Measure PV
3 Circulate $\text{CO}$ over Ascarite or remove to pump		6 Add measured amount of $\text{H}_2$ in excess required to combine with the oxygen measure total PV
4 With manometer closed remove dry ice—measure PV— $\text{H}_2\text{O}$		7 Circulate gas over hot platinum ribbon and magnesium perchlorate Measure PV $\Delta\text{PV} = \frac{1}{3}\text{O}_2$ $\frac{2}{3}\text{H}_2$
		8 Circulate gas over Ascarite Measure PV $\Delta\text{PV} = \frac{1}{3}\text{O}_2$ $\frac{2}{3}\text{CO}$
		9 Circulate over copper oxide $320^\circ\text{C}$ and magnesium perchlorate Measure PV $\Delta\text{PV} = \text{H}_2$
		10(a) Circulate over Ascarite Measure PV $\Delta\text{PV} = \text{CO}$
		(b) Residual PV $\text{N}_2$ — $\text{CH}_4$
		11 Transfer gas to combustion pipet, add excess oxygen to combine with $\text{CH}_4$ , compress to small volume and spark
		12 Circulate over magnesium perchlorate Measure PV $\text{PV} = \text{N}_2$ , $\text{O}_2$ , $\text{CO}_2$
		13 Circulate over Ascarite Measure PV
		14 Residual PV (step 10(b)) minus $\text{CH}_4$ (Step 13) = $\text{N}_2$

\* For description of method, see footnote 10, p 1565

in part. Initially, in the study of unknown samples, it is advisable to collect the gas in a sample bottle for analysis with a mass spectrometer. In this way the chemist can select the proper scheme of analysis. Also, the residual or inert gas should be identified by the mass spectrometer.

## INJECTION OF METAL SAMPLES INTO A VACUUM STATION

One of the advantages of vacuum techniques is that the sample or samples can be placed within the vacuum analytical station. After the apparatus has been properly conditioned, the sample can be injected into the furnace for analysis. In Fig. 36-1 and Fig. 36-2, sample loading arms for magnetic materials are shown.

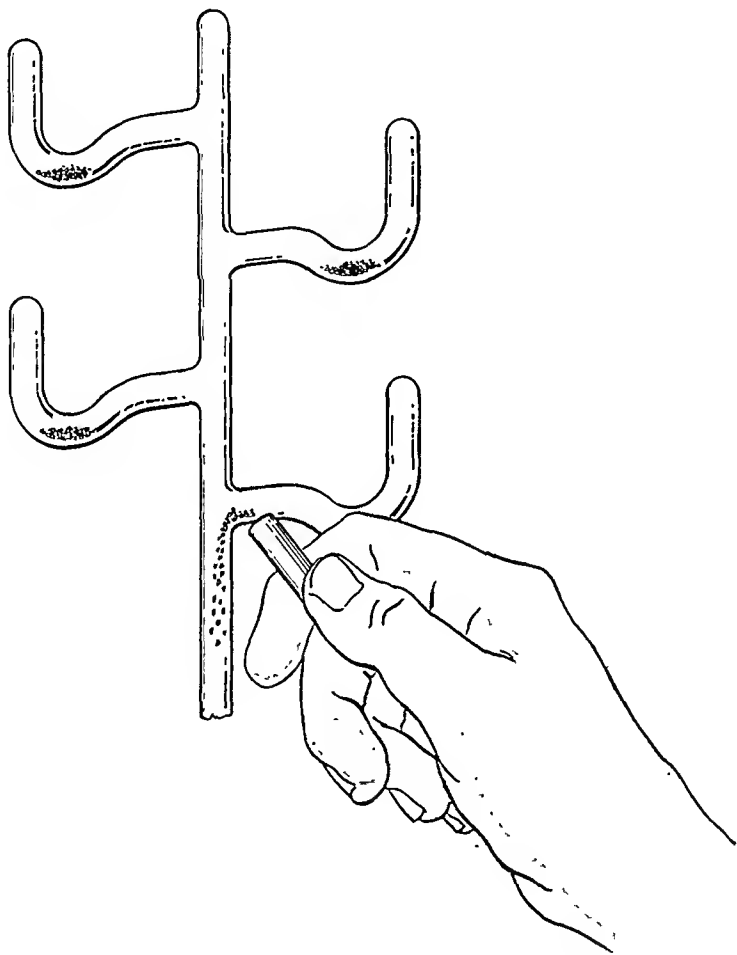


FIG. 36-1. Sample Loading Arm for Magnetic Materials.

The metal sample is weighed and placed in one of the glass sidearms as shown, and then the glass tube is sealed off with a torch. Several samples can be loaded in the sidearms, and can be injected into a furnace for analysis when desired.

When the sample material is nonmagnetic, it is placed in a magnetic cup, as shown in Fig. 36-3. This cup, made of iron, nickel, or Kovar, is lifted by means of a magnet. In this manner the cup is withdrawn from the sidearm and pulled to a position for dumping the sample. Figure 36-4 shows a technique for injecting

nonmagnetic samples. An iron slug is enclosed in a glass tubulation. By means of two platinum wires this tubulation is attached to a magnetic material that can be lifted up over a sample by means of a magnet. The sample can then be pushed forward into the furnace. The advantage of this unit is that the next sample cannot work into the furnace as a result of vibration.

In some cases to admit a sample after the analytical station is under vacuum is an advantage. This is necessary in determining hydrogen in steel, for example.

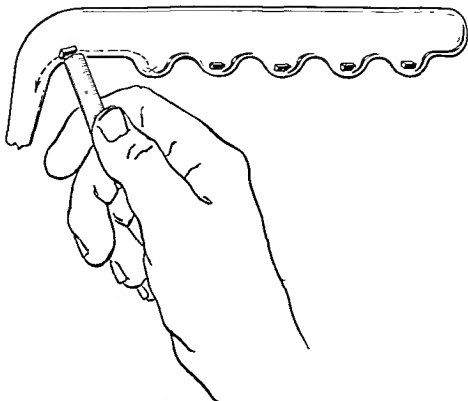


FIG. 36.2 Sample Loading Arm for Magnetic Materials

since hydrogen will diffuse from steel when held under vacuum. Also, an additional sample can be admitted to the vacuum station and then analyzed immediately. This is a distinct advantage when the apparatus is used for control work. When the sample is not readily wet or alloyed with mercury, it may be admitted into the vacuum station through a mercury lift, Fig. 36.5. When the apparatus is evacuated the mercury rises in the tube to the barometric height, which is almost up to the sidearm. To introduce a sample into the station, pick up the sample with a pair of tweezers, immerse it in the mercury and under the vertical tube. When the sample is released, it will float to the top of the mercury column. Then it can be moved readily, with a bar magnet, to any desired position.

A magnetic or nonmagnetic sample can be admitted to a vacuum station through a vacuum lock<sup>11</sup> as shown in Fig. 36.6. With the stopcock,  $S_1$ , closed, stopcock,  $S_2$ ,

<sup>11</sup> Also refer to the vacuum lock described in "Use of Stopcocks to Provide a Vacuum Lock," below, p. 1590.

is opened to air to release the vacuum. The standard tapered joint, which has been waxed leak-tight with Apiczon wax "W," is warmed with a soft Bunsen flame and removed. The sample is placed in a glass boat, which is fused to a glass-enclosed magnetic slug. The boat is inserted into the sidearm; the joint is replaced and sealed by warming the wax again, and with rotation under slight pressure.

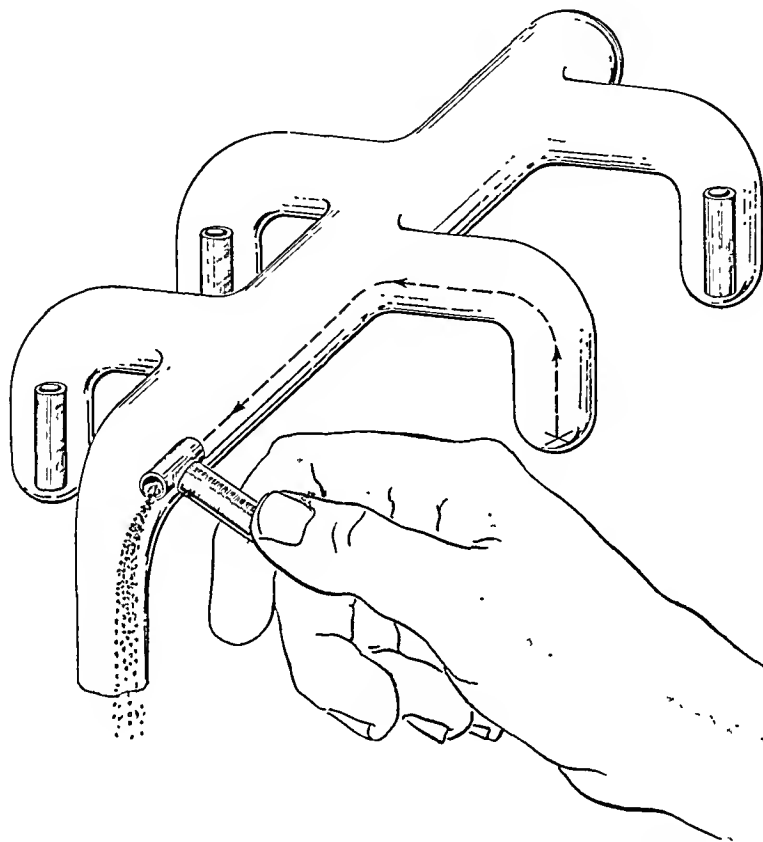


FIG. 36-3. Sample Loading Arm for Nonmagnetic Materials.

When the wax is cool, turn stopcock  $S_2$  to auxiliary vacuum. After evacuation, close  $S_2$  and open  $S_1$ . By means of the magnet, push the boat containing the sample through the hole in the stopcock, and then rotate it to dump the sample out of the boat and into the analytical station. The boat is withdrawn, and  $S_1$  is closed. This technique permits the admission of a sample to an evacuated system at any time without danger of contamination from stopcock grease.

### ADMISSION OF GAS TO AN EVACUATED SYSTEM

It is often necessary to admit small amounts of gas to an evacuated system. Because the pressure differential is considerable, 1 atm. or more, several basic schemes have been devised for admitting small amounts of gas, and eliminating the danger

of surging the mercury in the vacuum system. Figure 36-7 shows a very convenient method for admitting a few cc mm of gas to an evacuated system. Most gas companies can supply 1 liter bottles of gas at a pressure of 1 atm with breakoff tips. To this bottle is sealed a tube containing a lavite plug  $\frac{1}{4}$  in. in diameter by  $\frac{1}{8}$  in. long. When the gas is purchased in a soft lead glass bottle the lavite plug and assembly can be sealed to the bottle directly. A similar lavite plug is sealed

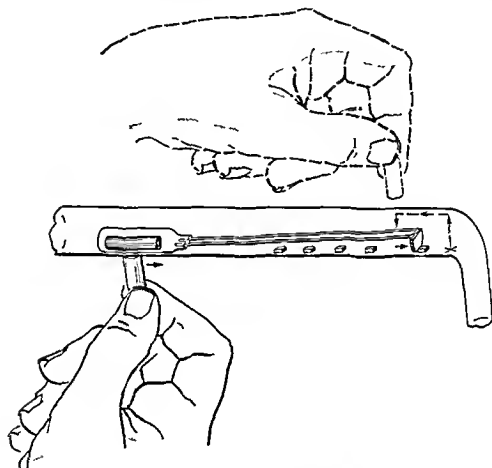


FIG 36-4 Apparatus for Injecting Nonmagnetic Materials

into a lead glass tube and by means of a 7 step seal is attached to the hard glass analytical station. As shown the 2 plugs are separated by mercury. Initially the air is evacuated between the breakoff tip and the lavite plug. Then by means of a gas torch seal off the glass restriction. Raise the glass enclosed iron slug and allow it to drop on the fragile tip to release the gas from the bottle. When gas is desired in the vacuum system raise the gas bottle until the 2 lavite plugs are in physical contact. Gas will slowly diffuse into the vacuum station until the bottle is lowered to permit the mercury to act as a cutoff.

Another very simple means of admitting a small amount of gas to an evacuated system is shown in Fig 36-8. A special dosing stopcock  $S_1$  is constructed, in which the bore of the plug does not extend all the way through. The volume of this



cavity can be calibrated. This stopcock is sealed to a gas bottle, *A*. With the stopcock closed, evacuate the volume between the bottle and the stopcock, and seal off the glass restriction, *C*, with a torch. Then, raise the slug, *B*, with a magnet, and let it fall to fracture the glass tip. Gas is admitted to the evacuated system by rotating the plug. The pressure is measured with the manometer, *D*.

A simple but practical way of admitting a small amount of gas to an evacuated system is shown in Fig. 36-9. The advantage of this technique is that a known

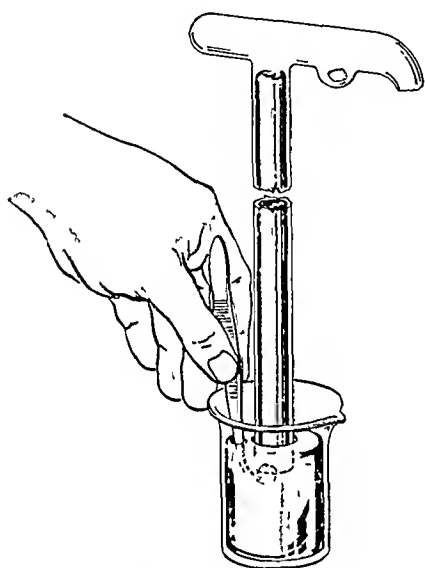


FIG. 36-5. Mercury Lift.

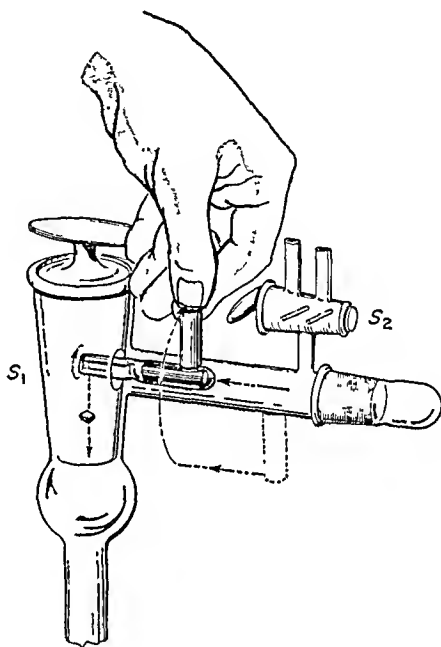


FIG. 36-6. Vacuum Lock.

quantity of gas can be admitted simply by calibrating the volume between the 2 stopcocks. Close  $S_1$  and open  $S_2$  to evacuate. Then, close  $S_2$ , open  $S_1$  to draw air or a gas volume at known pressure. Close  $S_1$  and open  $S_2$  to the vacuum apparatus. In this way a known quantity of gas at temperature  $T$  is admitted.

$$Q_{cc\text{ mm.}} = P_{mm.} V_{cc.}$$

In many instances, such as in gas sorption studies, it has been found necessary to admit gas at a slow and controlled rate from a reservoir, attached at *A* in Fig. 36-10, to an evacuated system, attached at *B*. This technique uses a porcelain leak similar to that described by Smythe<sup>12</sup> and Hagstrum and Weinhart.<sup>13</sup> As shown in Fig. 36-10, a porous porcelain rod, through which the gas leaks from the reservoir, is about .055 in. in diameter, and 5 in. long. The leak is an underfired material, which can be obtained from Stupakoff Ceramic Co. It is sealed to a short section of No. 542 blue glass, which in turn is sealed to 7740 Pyrex. The leak assembly

<sup>12</sup> Smythe, W. R., *Rev. Sci. Inst.* 7, 435, 1936.

<sup>13</sup> Hagstrum, H. D., and Weinhart, H. W., *ibid.*, 21, 394, 1950.

is sealed to a mercury well at *C* to permit adjustment of the mercury level. The resistance offered to the gas flow is proportional to the length wetted by the mer

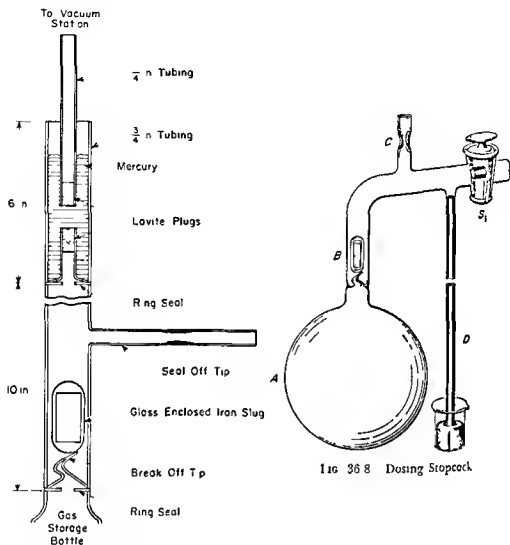


FIG. 36.7 Admission of Gas to an Evacuated System

cury and glass seal at the bottom of the rod. Molnar and Hartman<sup>14</sup> determined the leak rate of this unit to be

$$\frac{(1 \times 10^{13})p}{l} \text{ molecules per second for nitrogen}$$

where  $l$  is expressed in centimeters and  $p$  is the pressure in millimeters of mercury

<sup>14</sup> Molnar J. P. and Hartman C. D. Rev. Sci. Instr. 21, 395, 1950

in the gas bottle. This flow rate depends on the outlet pressure being negligible as compared to the inlet pressure.

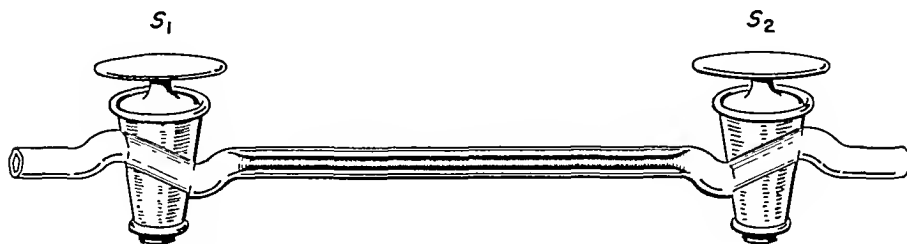


FIG. 36-9. Admission of Gas from Capillary Volume.

More recently, Morrison<sup>15</sup> described a technique for admitting gas to an evacuated system that is based on the same principle using the porcelain leak, but has several unique features. The advantages of this system are that the leak rate can be controlled in the range of 10,000 to 1; long mercury columns, to compensate for pressure differentials, are not required; gas reservoirs are used at atmospheric pressure; and the leak rate is held constant for many hours. As shown in Fig. 36-11, the apparatus consists of 2 leaks, each containing a porcelain rod of different diameter, in order to obtain a wide range of leak rates. In addition, the small diameter rod in leak No. 2 was ground to a tapered point. In this way a high capacity and wide flow range are obtained by using the 2 leaks and 2 reservoirs in series. The first leak controls the pressure in a volume between the 2. This volume is set at a high or low pressure depending on the leak rate desired, the pressure being measured with a Pirani gauge. The leak rate is proportional to the pressure and the length of porcelain exposed to the gas. The mercury level about the leak can be changed by raising the glass skirt up or down in the mercury well. Initially the system is evacuated to a low pressure by pumping through the stopcocks,  $A$  and  $B$ , which open a bypass of the leaks. After evacuation, close  $A$  and break the tip on the gas reservoir by raising the slug with a magnet and letting it fall. Close stopcocks,  $B$  and  $C$ , and raise the plunger by means of a solenoid in the first leak to expose the porcelain rod to the gas. The pressure is adjusted in the intermediate reservoir and measured with a Pirani gauge. Then, leak No. 1 is cut off, and leak No. 2 is adjusted to the desired rate of flow. Such an apparatus

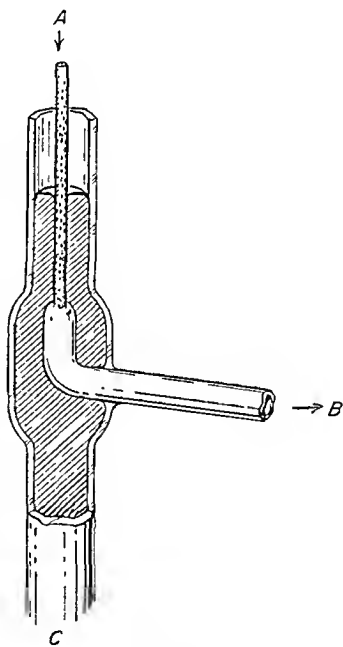


FIG. 36-10. Porcelain Leak. (Courtesy The Review of Scientific Instruments, American Institute of Physics, New York.)

<sup>15</sup> Morrison, J., *Rev. Sci. Inst.*, 24, 230, 1953.

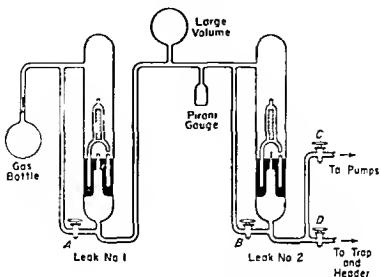


FIG. 36-11 Apparatus Consisting of 2 Leaks

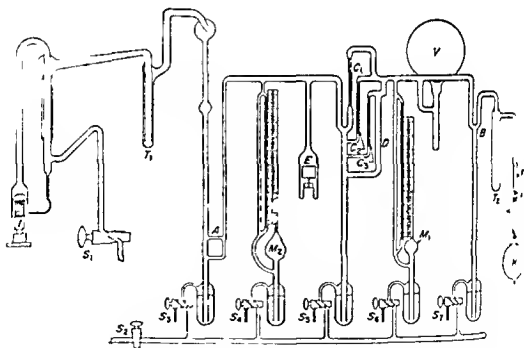


FIG. 36-12 Capillary Leak for Admission of Gas to an Evacuated System at a Controlled Rate (Reproduced in part with permission of the copyright owner, The Electrochemical Society, Inc., New York)

is very useful in determining the amount of gas sorbed by metals or evaporated metal films.

A capillary leak<sup>16</sup> for admitting gas to an evacuated system at a controlled rate is shown in Fig. 36-12. After evacuation of the entire apparatus to the main pump connected to  $S_1$ , the mercury is raised in the capillary column to the point of cutoff by opening  $S_5$  to air. Gas is admitted to the 5-l. volume,  $V$ , to a desired pressure by raising the gas bottle,  $H$ , to permit the gas to diffuse through the ceramic plugs. The mercury is raised to the level of cutoff at  $B$ . Then the pressure is measured by the McLeod gauge,  $M_1$ . The gas is admitted from  $V$  to the vacuum section containing the sample,  $E$ , at a desired rate, by means of the capillaries. This is accomplished by opening stopcock  $S_3$  to a manifold connected to the auxiliary vacuum at  $S_2$  to lower the mercury to a level so that the gas will flow from  $V$  through capillary  $C_1$ ,  $C_1$  plus  $C_2$ , or  $C_1$  plus  $C_2$  plus  $C_3$ . Each capillary is about 13 cm. long and .06 cm. I.D. The capillary,  $C_1$ , is calibrated by admitting pure dry gas to  $V$  until the pressure is about 0.1 mm. The mercury level in the capillaries is then lowered so that the gas leaks from  $V$  through  $C_1$  to pump. The pressure drop in  $V$  is measured as a function of time. Repeat this procedure for  $C_1$  plus  $C_2$  and  $C_1$  plus  $C_2$  plus  $C_3$ . The rate of flow,  $Q$ , of a perfect gas from volume,  $V$ , at pressure,  $P_1$ , is experimentally determined from

$$Q = -\frac{d(p_1 V)}{dt} = -\frac{V dp_1}{dt}$$

where  $Q$  is in cc. mm. per minute when  $p_1$  is expressed in millimeters, and  $V$  in cubic centimeters. For pure diffusion flow<sup>17</sup>  $\frac{dp_1}{dt}$  is a simple function of  $p_1$  when  $p_2$ , the pressure on the pump side, is much less than  $p_1$ , i.e.,

$$-V \frac{dp_1}{dt} = \gamma p_1$$

where  $\gamma$  is the pumping admittance of the capillary, and is a function of the temperature and molecular weight of the gas. Integrating,

$$\log_{10} p_1 = \log_{10} p_0 - \frac{\gamma}{2.3V} (t - t_0)$$

where the subscript zero designates initial values of  $p_1$  and  $t$ . Thus the admittance,  $\gamma$ , of the capillary is determined from the slope of the straight line obtained from a plot of  $\log_{10} p_1$  vs.  $t$ . Then  $Q = \gamma \cdot p$  cc. mm. per minute. After the capillaries have been calibrated for 1 gas, the admittance,  $\gamma$ , may be calculated for any other ideal gas, since  $\gamma$  varies inversely with the square root of the molecular weight. Thus

$$\frac{\gamma_2}{\gamma_1} = \frac{\sqrt{M_1}}{\sqrt{M_2}}$$

<sup>16</sup> Guldner, W. G., and Wooten, L. A., The Sorption of Gases by Zirconium, J. Elec. Chem. Soc., 93, 223-35, 1948.

<sup>17</sup> Dushman, S., Production and Measurement of High Vacuum, General Electric Review, Schenectady, N. Y., 30-33, 1922.

In normal use the pressure in  $V$  is recorded after 1 hr 30 min or 20 min depending on the number of capillaries in use

### DEVICES FOR OBTAINING GAS FROM CLOSED CONTAINERS

Very often the application of a good mechanical device for collecting gas from a sample contained in a glass or metal envelope is the first step toward a successful experiment. Many ingenious devices have been described.

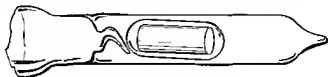


FIG. 36.13. Fragile Break Off Tip

The use of a fragile tip or thin walled bulb has been described<sup>18, 19</sup> and is shown in Fig. 36.13. These fragile tips can be attached initially to a manifold for collecting gas to a vacuum tube or to a similar device for collection of a gas sample. This tubulation may be sealed to an analytical station and the gas released when desired by simply breaking the tip with the glass enclosed metal slug.

In Fig. 36.14 a rotating stopcock<sup>20</sup> is used for fracturing a fragile tip. A tube containing the gas sample consists of a thin walled tip which may be lightly marked with a file scratch. The tube is inserted at  $A$  and waxed with Apiezon wax  $W$  or similar high vacuum wax. The fragile tip is broken off by simply rotating the stopcock. The eccentric end of the stem exerts a side pressure on the fragile tip to the point of fracture.

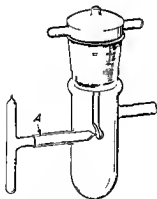


FIG. 36.14. Rotating Stopcock for Fracturing Tip

In many gas studies it has been found necessary to obtain gas from a glass envelope or vacuum tube. In some cases this can be readily accomplished by dropping a metal slug on a grid or seal off tip.<sup>2</sup> Stronger envelopes are broken readily in the apparatus shown in Fig. 36.15. In this apparatus<sup>2</sup> the vacuum tube is placed in the metal to glass envelope. The tapered joint is waxed vacuum tight with Apiezon wax  $W$ . The tubulation is evacuated and the stopcock is closed. The copper or steel outer tube is squeezed in a vise to break the glass envelope. Steel tubing 2.5 in. in diameter 18 in. long 0.010 in. wall thickness and copper tubing with a 0.030 in. wall have been found satisfactory. Figure

<sup>18</sup> Farkas, A. and Mehille, H. W. *Experimental Methods in Gas Reactions*. Macmillan, London, 148, 1939.

<sup>19</sup> Barr, W. E. and Anhorn, V. J. *Scientific and Industrial Glass Blowing and Laboratory Techniques*. Instruments Publishing Co. Inc. Pittsburgh, 245, 1949.

<sup>20</sup> Sanderson, R. T. *Vacuum Manipulation of Volatile Compounds*. John Wiley & Sons, Inc. New York, 67, 1948.

<sup>21</sup> Morrison, J. *Gas Collection and Analysis System in Vacuum Tube Problems*. Vacuum Symposium Transactions, 1947.

<sup>22</sup> Norton, F. J. *Rev. Sci. Inst.* **26**, 238, 1955.

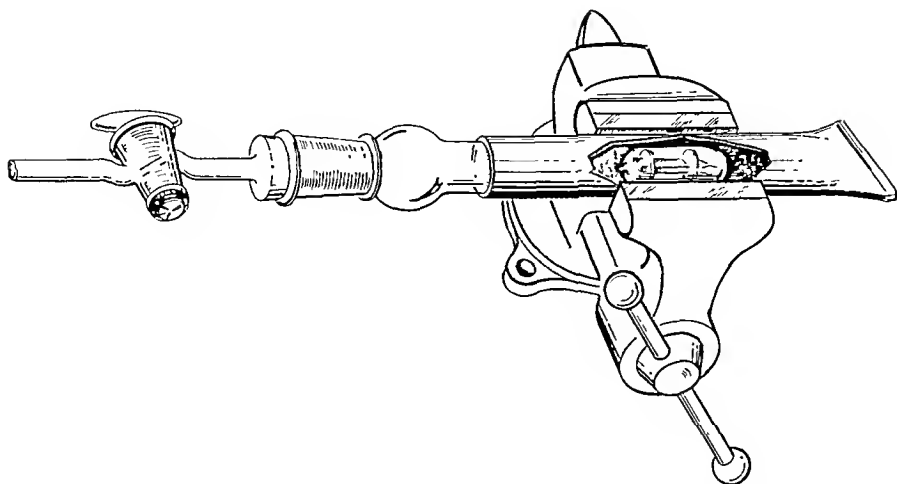


FIG. 36-15. Vacuum Tube Opener. (Courtesy The Review of Scientific Instruments, American Institute of Physics, New York.)

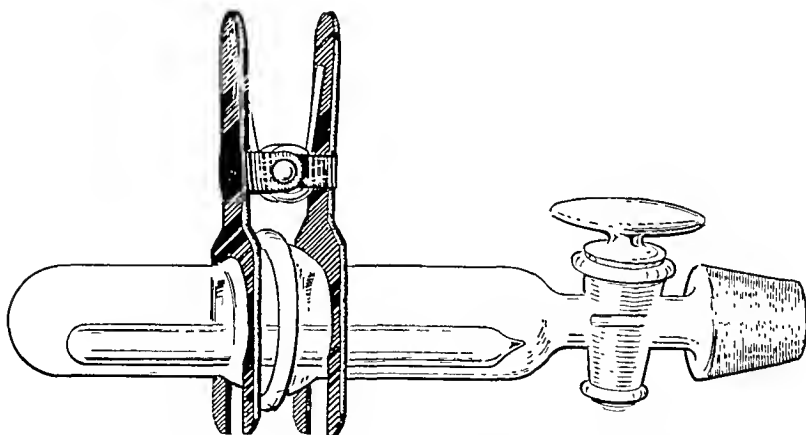


FIG. 36-16. Glass Ball Joint for Fracturing Glass Tubes.

36-16 shows a device<sup>23</sup> for breaking tubulations by means of a glass ball joint. This unit may be constructed in various sizes. The inner sample tube is broken by flexing the greased ball joint through a small angle. In a similar manner a metal bellows which is attached to the vacuum station with glass to metal seals is used.

A very functional unit for fracturing a glass tip is shown in Fig. 36-17. This apparatus makes use of a ball type vacuum metal valve (manufactured by Vacuum Electronic Engineering Co., L. I., N. Y.). The lateral motion of this valve is car-

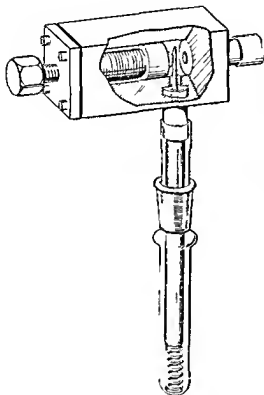


FIG. 36-17 Metal Valve for Fracturing Glass Tubulations

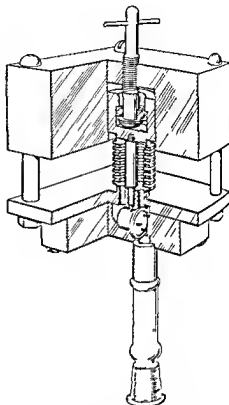


FIG. 36-18 Metal Punching Device for Metal Encapsulations

ried out by means of a screw acting on a ball valve. Leakage about the screw mechanism is prevented by operating inside a metal bellows. The glass tip on the device projects into the valve between the ball and seat and is held in place by means of a spring located at the bottom of the glass envelope. The glass envelope is designed to fit the device under test so as to minimize the dead space volume.

Since many devices are in metal containers, i.e., vacuum tubes, transistors, condensors, relays, and switches, the chemist is often confronted with the problem of determining the gas content or purity within the envelope. In many cases the dead space volume in the device is very small, which means that a vacuum-tight sampling technique must be used. Figure 36-18 shows a mechanical unit that is capable of piercing the steel can with a needle to release the gas for analysis.

<sup>23</sup> Norton, F. J., *Rev. Sci. Instr.* **20**, 670 (1949).

<sup>24</sup> Francois, E. E., and Becker, E. J., Memorandum for File, Bell Telephone Laboratories, 1959.



This unit was designed for piercing, under vacuum, the envelope of miniature electron devices, which have a total volume of about 5 cc. A Sylphon bellows is employed as a vacuum-tight shield that will permit the translation of the piercing motion. The turnpost is attached to the inner race of the bearing, and screws through the piston housing. When the turnpost is screwed through the piston housing, a force is translated to the needle to pierce the shell of the electron device. After piercing the can, the needle is withdrawn to allow the gas to be pumped out for analysis. The next sample can be readily inserted by removing 4 screws in the end plate. Units of larger dimensions may be pierced for analysis in a similar manner.

A device<sup>25</sup> for breaking open sealed electronic devices is shown in Fig. 36-19. Steel rods *A* and *B* are fitted to slide easily within the glass sidearms. The solenoids *C* and *D* are wired to activate simultaneously. Rod *B* is pulled up sharply to rap the glass envelope, and at the same time, rod *A*, which was resting on the glass, is pulled downward. In this way, the envelope is more effectively broken with a minimum of shock to the apparatus. After the solenoids are de-energized, rod *B* drops back on the coil spring. Several variations of this design have been used; for example, a needle point has been used to pierce a metal envelope.

In some studies, it is necessary to devise a means of drilling under vacuum to release gas from a hole or blister in the metal, or from an extremely heavy walled unit. The selection of the best means for accomplishing this depends upon the amount of gas encountered and the precision desired. Rotational seals for drilling have included lubricated ground joints or shafts, and rubber or plastic materials such as "O" rings under compression. The drilling may be carried out in an inert gas to minimize contamination from leaks, and then the total gas is collected for analysis. Figure 36-20<sup>26</sup> shows a scheme where the surface tension of liquid metal is utilized in making high vacuum seals about a rotating shaft. Here, the eutectic alloy of Ga, In, and Sn, which is molten at room temperature and has an extremely low vapor pressure, is used.

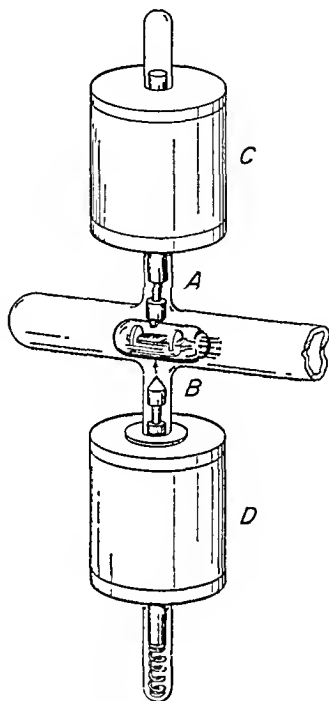


FIG. 36-19. Use of Solenoids for Fracturing Glass Enclosures. (Courtesy The Institute of Physics and the Physical Society, London, England.)

<sup>25</sup> Charlton, M. G., and Perkin, G. M. C., Method for Breaking Open Sealed Electronic Devices in Vacuo, *J. Sci. Instr.*, 36, 49, 1959.

<sup>26</sup> Milleron, N., Utilization of the Surface Tension of Liquid Metals in Making High-Vacuum Seals, *Vacuum Symposium Transactions*, Pergamon Press, Inc., Oxford and New York, 38, 1957. Figure 36-20 is reproduced with permission of the copyright owner.

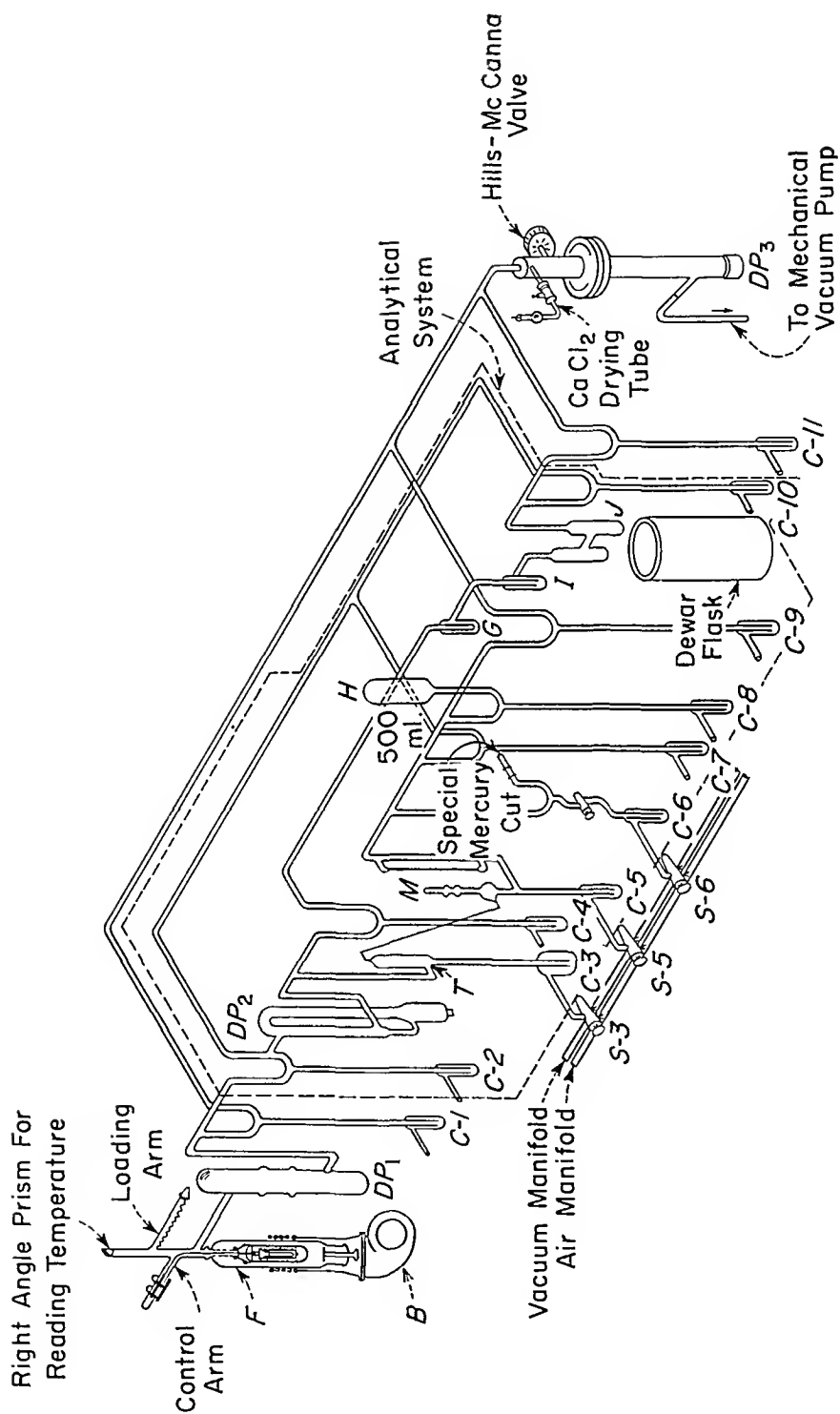


FIG. 36-21. Vacuum Fusion Apparatus. (Courtesy National Research Corp., Cambridge, Mass.,)

shown in complete detail in Fig. 36-22. The furnace body is constructed of boro silicate glass and consists of a removable glass ground joint at the bottom side arms for magnetically lifting the graphite plug from the crucible and for injecting the metal samples. An optical flat to permit the measurement of the temperature in the crucible by means of an optical pyrometer and an evacuation port which is connected to the high speed collecting mercury diffusion pump

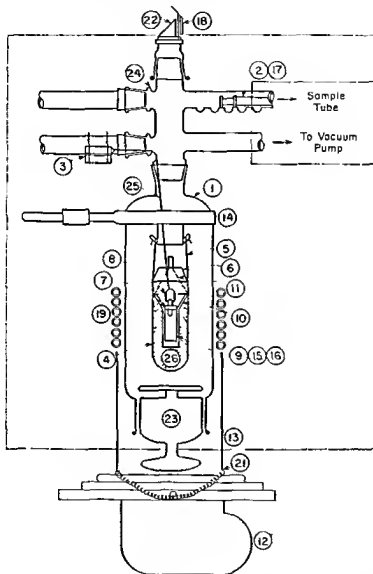


FIG. 36-22 Vacuum Fusion Furnace (1) Glass Furnace Body (2) Specimen Pusher (3) Magnetic Control (4) Quartz Tube (5) Crucible Wires Platinum (6) Crucible Cap (7) Crucible Plug (8) Crucible Plug Handle (9) Crucible (10) Funnel (11) Funnel Lid (for loading only) (12) Blower Assembly (13) Blower Air Guide (14) Furnace Clamp (15) Crucible Fork (for introducing sample) (16) Crucible Remover (for removing crucible) (17) Loading Pusher (18) Sight Glass Radiation Shield (19) Induction Coil (20) Graphite Powder (21) Spring (22) Prism Assembly (23) Lower Furnace Plug (24) Furnace Head Only (25) Molybdenum Wire 6035 in by 5 ft long (26) Graphite Powder

Within the furnace, a clear quartz or Vycor tube is supported. It is suspended from the glass ears on the injection tube by platinum wire hooks, .050 in. diameter wire, which hook into 2 holes in the quartz tube located diametrically opposite. Within the quartz tube, a graphite crucible floats in graphite powder, the crucible being the conductor for the high frequency induction heating, and the graphite powder, the insulator.

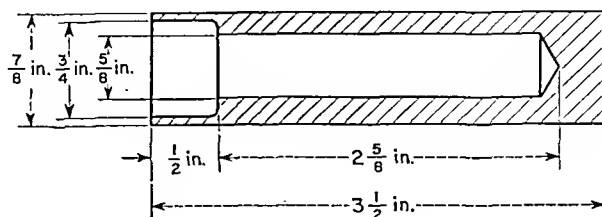


FIG. 36-23. Graphite Crucible.

**Loading the Crucible Assembly.**—Place about 1 1/2 in. of sub-250 mesh, AUX halogen treated, graphite powder (obtainable from United Carbon Co., Bay City, Michigan) in the bottom of the quartz tube; insert the graphite crucible, Fig. 36-23, into the graphite powder being careful to keep the walls of the crucible coaxial to those of the quartz tube; place a metal or glass cover over the crucible to keep powder from falling into the crucible and act as a jig for centering it in the quartz tube; and pour in graphite powder until it reaches the top of the crucible. Remove cover and insert the graphite funnel, Fig. 36-24. Replace cover, and add graphite powder until it reaches the top of the graphite funnel. Remove cover, insert a glass tube into the crucible, and blow out any powder. When it is necessary to avoid excessive spattering of metal to the furnace walls, place the Vycor shield on top of the quartz tube so that the notches in the base fit over the platinum wires. All precautions must be used to avoid packing of the graphite powder, through excessive tapping or vibration. This will cause poor insulation and difficulty in evacuation, i.e., powder will blow out during evacuation or initial heating.

**Assembling the Furnace.**—Insert the hooks of the lifting rod, Fig. 36-25, into the 2 loops of the platinum wire, and carefully lift the assembly into place, making sure that the platinum loops are secure over the glass ears of the injection tube. Adjustments to the platinum wires may be required to make the assembly hang straight in the furnace. Removal of this assembly is carried out by means of the crucible remover shown in Fig. 36-26. At the bottom of the furnace, warm the inner joint in a soft Bunsen flame, and apply a thin uniform coat of Apiezon wax "W." Warm the outer-joint; insert the waxed joint, and rotate it with light pressure until it is well seated. Hold the plug tightly in place until the wax has cooled. Adjust the induction heating coil so that the top coil is at the same level as the top of the graphite crucible.

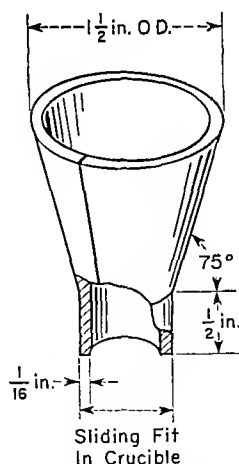


FIG. 36-24. Graphite Funnel.

sifted to remove the dust, and outgassed initially at 230°C. for several hours in vacuum to remove the water vapor. This reagent is used at room temperature. Thereafter, only short periods of outgassing are required after the reagents have been exposed to dry air during a loading period.

Both reagents are heated by means of Glascol heaters that surround the glass traps. The temperature of these traps is measured with an iron-constantan thermocouple, which is connected to a low resistance microameter.

*Liquid Nitrogen.*—Liquid nitrogen is used about the double trap, *J*, to freeze out the condensable gas, carbon dioxide. In some areas where liquid nitrogen is not readily available, Ascarite is used to remove the carbon dioxide. This reagent should be baked at 200°C. prior to use. It is then used for analysis at room temperature.

*Induction Heater and Coil.*—The graphite crucible is heated by means of a high frequency vacuum tube oscillator, about 2 kw. output with a frequency of 350 to 500 kc. The heater coil consists of 11 turns of  $\frac{1}{4}$  in. copper tubing, closely wound and cooled with water. The coil has an inside diameter of about  $3\frac{1}{2}$  in., which provides adequate clearance about the glass furnace.

*Evacuation of the Apparatus.*—In the evacuation of the apparatus, the mercury in the cutoff columns will rise. This rise is counteracted by means of a rough secondary vacuum to keep the mercury far below the points of cutoff, and to allow adequate degassing of the glass walls. The 3-way stopcocks connect the apparatus to the secondary vacuum to lower the columns, and can be turned to air to permit the mercury to rise in the columns.

To evacuate the system, close the Hills-McCanna main valve located between the apparatus and main pump, turn all 3-way stopcocks to the horizontal position and open to air, close air release valve above  $DP_3$ , and turn on the mechanical pumps. With extreme caution, open main valve above diffusion pump very slowly until the mercury begins to rise in the columns. Continue to evacuate slowly for at least 10 min. If the pumpdown is too rapid, the carbon powder will fluff and may be blown about the system. Keep all mercury columns below the point of cutoff by periodically turning the 3-way stopcocks to the secondary vacuum. This is especially true in  $C_3$ ,  $C_5$ , and  $C_6$ . When no further upward movement of mercury in the tubes is visible, and the pressure is less than 1 mm. (a reading of 200 on the quadratic scale of the McLeod gauge), open main valve fully. Turn on water for diffusion pumps, induction coil, and electronic heater. Then turn on heaters for the diffusions pumps. After about 1 hr., no pressure should be observed when a reading is taken with the McLeod gauge.

*Outgassing the Crucible.*—It is essential that the graphite crucible and powder be outgassed very slowly to avoid fluffing out the graphite powder. Turn on the air blower for the furnace, and very slowly advance the power of the oscillator until the crucible reaches a temperature of about 2500°C. (One hr. temperature rise required for safe evacuation.) Continue heating at 2500°C. for 2 to 3 hr., or until a tolerable blank has been obtained.

*Blank.*—The blank determination consists of the amount of gas evolved from the system at a temperature and heating time of the sample. The maximum differential between outgassing and fusion temperature is desired. The temperature required for fusion is dependent on the melting point of the metal being analyzed and the fusion bath. Most analyses are made between 1650° and 1900°C.

It has been found that 20 min. is adequate for collecting the gas from a sample,

and that the time never exceeds 30 min. A suitable blank should be of the order of 5 cc mm of gas for 30 min at 1650°C. Small blanks can be obtained with extensive care and the significance minimized by increasing the sample weight.

**Outgassing of Reagents**—Outgas reagents at temperatures described under reagents until little or no blank is obtained. Use the copper oxide mixture at 325°C and the magnesium perchlorate at ambient.

**Collection of Gas Blank**—Check the pressure with the McLeod gauge to be sure the system has a good vacuum; close all mercury cutoffs except  $C_1$ ; raise the temperature of the crucible to operating or fusion temperature and turn on time switch (fusion time 20 to 30 min). Immediately close  $C_1$  and  $C_3$ , open  $C_2$  and lower the mercury in the Toepler pump  $T$  below the bulb. When the timer buzzes close cutoff  $C_2$  and open  $C_1$ . Adjust the mercury level in the McLeod gauge to a point just below the bulb that is between the point of cutoff and the capillary input from the Toepler. Pump the gas with the Toepler pump into the McLeod gauge until further pumping shows no increase in pressure. The Toepler is operated by opening the 3 way stopcock  $S_3$  to air which lets the mercury rise in the bulb and forces the gas over into the McLeod gauge. When the mercury spills over into the gauge the stopcock is opened to vacuum until the mercury is again below the Toepler bulb. Then this cycle is repeated until all the gas is collected. Measure the pressure. Analyze as described below.

**Analysis of Sample for Oxygen, Hydrogen and Nitrogen**—The analysis of a sample for oxygen, hydrogen and nitrogen should be carried out at the same time and temperature as for the blank.

Evacuate the residual gases in the Toepler pump after the analysis of the blank and return mercury from  $C_2$  to  $C_1$  by opening  $S_3$  to air. Proceed for analysis of sample by closing  $C_1$ ,  $C_4$ ,  $C_7$ ,  $C_8$ ,  $C_9$ ,  $C_{10}$  and  $C_{11}$  and leave all other cutoffs open. The special mercury cutoff  $C_6$  for addition of gases is left in cutoff position always unless otherwise prescribed.

Adjust the furnace temperature for fusion as indicated by an optical pyrometer and adjust timer to the same time as that used for the blank. Inject sample from loading arm either by a magnet or a magnetic pusher and collect gas as described under blank. Measure  $P_V$  collected. (Refer to Methods of Measurement below p. 1587.)

To make an analysis close cutoff  $C_2$ ; raise the mercury in the Toepler pump above the point of cutoff; open cutoffs  $C_4$  and  $C_7$  and raise the Dewar flask containing liquid nitrogen about the cold traps. Then lower the mercury in the McLeod gauge below the point of cutoff to permit the gas to be pumped out by the mercury diffusion pump and over the reagents. After about 3 min check the McLeod gauge reading until no differential is detected and raise the mercury in the McLeod gauge just above the point of cutoff. Open cutoff  $C_{10}$  to allow the gas to be recirculated over the reagents by means of the diffusion pump. After circulating the gas for at least 5 min, the time for a specific apparatus being dependent on the sensitivity of the reagents and the amount of gas present close cutoff  $C_4$  and lower the mercury in the Toepler pump below the point of cutoff. After about 5 min pump the gas with the Toepler into the McLeod gauge until a constant reading is obtained. Record value which is a measure of the nitrogen. Leave the gas in the McLeod gauge with the mercury just above the point of cutoff and remove the Dewar flask from the cold traps. With the Toepler pump open as before wait about 10 min and then pump the carbon dioxide into the McLeod until the reading is constant. The gain over the nitrogen value is a measure of

the carbon dioxide. The total gas evolved by the sample, less the nitrogen and carbon dioxide, provides a value for the hydrogen. The values on the analysis of the gas sample are all corrected by a similar analysis of the blank.

**Analysis for Oxygen and Nitrogen (Only).**—In some instances, hydrogen is of no interest. Then, it is possible to shorten the time required for analysis in the following manner: check vacuum in the apparatus with a McLeod gauge, raise cutoffs  $C_1$ ,  $C_7$ ,  $C_8$ ,  $C_9$ , and  $C_{11}$ , and the mercury in the Toepler pump to point of cutoff; open  $C_2$ ,  $C_4$ ,  $C_{10}$ . This permits the gas evolved from the sample to bypass the Toepler pump and be circulated over the reagents, removing the hydrogen and freezing out the carbon dioxide in the cold traps. The general procedure described for complete analysis is repeated with the residual gas, nitrogen being collected and measured in the McLeod gauge. The carbon dioxide is then released as before and collected with the nitrogen. The difference in the amount is equal to the carbon dioxide. A blank determination is carried out in like manner and suitable corrections are applied.

**Analysis for Oxygen (Only).**—Proceed as described for oxygen and nitrogen except for the following modification. After the sample has been fused for about 10 min., and the bulk of the carbon dioxide has been collected in the cold traps, open cutoff  $C_{11}$ , which allows the residual gas nitrogen to be pumped out. At the end of the fusion period, close  $C_2$  and  $C_{11}$ , and collect and measure the amount of carbon dioxide in the usual manner. This procedure is not recommended for high precision work, since small losses may occur due to restricted recirculation over the reagents. Small amounts of carbon monoxide, which is the most difficult gas to oxidize with the copper oxide, might be lost as a noncondensable gas in conjunction with the nitrogen to pump.

**Analysis for Nitrogen (Only).**—When nitrogen is the only interest, proceed as described under oxygen and nitrogen. Pump the nitrogen with the Toepler pump into the McLeod gauge, and measure. Remove the Dewar flask from the cold trap, and open the cutoffs in the system for complete evacuation.

**Methods of Measurement.**—In this apparatus, the McLeod gauge, Fig. 36-28, is used for measuring the pressure. This gauge is unique for it can be used as a capillary pipet, a multi-range gauge with extra volumes, and with quadratic or linear scale.<sup>29</sup> The volumes of the capillary tubing per unit length and the bulbs

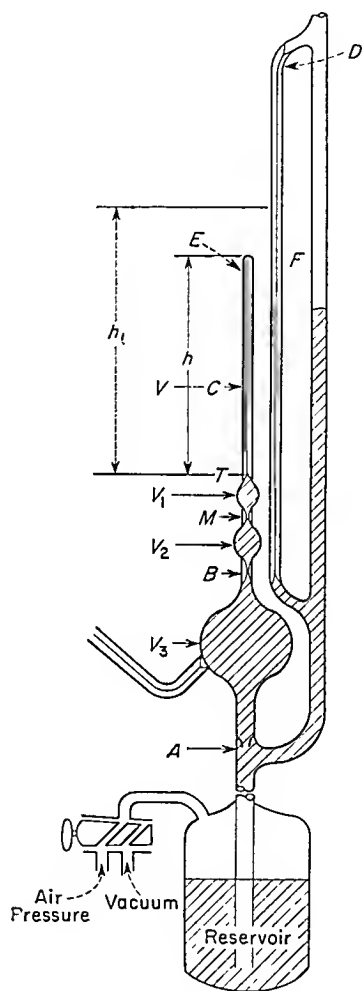


FIG. 36-28. McLeod Gauge.

<sup>29</sup> Dushman, S., *Production and Measurement of High Vacuum*, General Electric Review, Schenectady, N. Y., 1922; *Scientific Foundations of Vacuum Techniques*, John Wiley and Sons, Inc., New York, 1949.

*Gas Compressed to Point T.*

$$Q_{\text{cc. mm.}} = \frac{V}{V + V_1 + V_2 + V_3} \times h_1 \times V_T$$

where  $V_T$  is the total volume occupied by the gas, including the volume of the gauge and external volume or volumes.

*Gas Compressed to Point M.*

$$Q_{\text{cc. mm.}} = \frac{V + V_1}{V + V_1 + V_2 + V_3} \times h_1 \times V_T$$

*Gas Compressed to Point B.*

$$Q_{\text{cc. mm.}} = \frac{V + V_1 + V_2}{V + V_1 + V_2 + V_3} \times h_1 \times V_T$$

Calculations.—The quantity of each gas has been measured in units of  $PV$  (cc. mm.) and corrected by the blank. The percentage of each gas in the sample is calculated, at an ambient temperature of 25°C., as follows:

Nitrogen (measured directly as  $N_2$ )

$$\frac{\text{cc. mm.} \times 1.507 \times 10^{-4}}{\text{sample weight (grams)}} = N_2, \text{ per cent}$$

Oxygen (converted to CO and measured as  $CO_2$ )

$$\frac{\text{cc. mm.} \times 8.605 \times 10^{-5}}{\text{sample weight (grams)}} = O_2, \text{ per cent}$$

Hydrogen (converted to water vapor and adsorbed, hydrogen determined by difference)

$$\frac{\text{cc. mm.} \times 1.084 \times 10^{-5}}{\text{sample weight (grams)}} = H_2, \text{ per cent}$$

If the measurements are made at some temperature other than 25°C., the factor equivalent will change inversely, proportional to the ratio of the absolute temperatures,

$$\frac{T_{25}}{T_x}.$$

*Introduction of Samples to Apparatus While Under Vacuum.* Mercury Lift (for Non-Mercury Alloying Samples).—A mercury lift is shown in Fig. 36-5, and is used to admit a sample to the apparatus, which is already under vacuum. The lift consists of a glass tube attached to the sample loading arm, and extending down to an open vessel containing mercury. The column must be in excess of 760 mm. in height to prevent mercury from flowing into the sidearm. When the apparatus is under vacuum, the mercury rises through the open end of the tube up near the sample loading arm. To inject a sample, hold it in special nonalloying tongs, and slip it beneath the surface of the mercury and under the mercury column.



Release the sample and it will rise in the mercury column. Light samples may need coaxing with a magnet. When the sample reaches the top of the mercury column remove it by means of a magnet, to the loading arm after shaking off any globules of mercury. At the time of injection close  $C_2$  and open  $C_1$  to pump out any minute air occlusion. When the material is nonmagnetic, wrap the sample with iron wire having a known gas content. The principal need for a mercury lift is to obtain accurate results for hydrogen in steel. In a vacuum and at room temperature the bulk of the hydrogen in steel and a few other metals will diffuse out in a comparatively short time. Therefore the samples cannot be loaded in the side arm in the usual manner but must be injected through the mercury lift just prior to analysis.

Use of Jamesbury Valve <sup>30</sup>—A unique and practical way to admit samples to a loading arm while the apparatus is under vacuum is shown in Fig. 36-29. It is

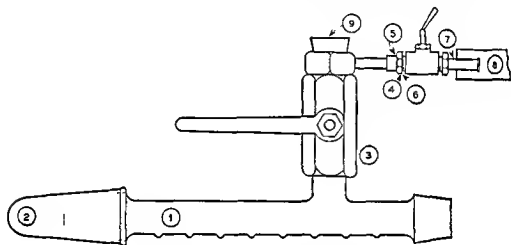


FIG. 36-29 Use of Jamesbury Valve

offered as an attachment for the vacuum fusion system and provides a means for admitting metal samples without the danger of contamination. The valve is ball type having a port large enough to admit the sample chunks. The metal stem and ball have seals adequate to hold a vacuum without lubrication.

To admit a sample to the loading arm remove rubber stopper 9, drop in the sample, replace the stopper, open valve 5 to secondary vacuum, and evacuate. Then close valve 5. With the crucible in the vacuum fusion furnace at room temperature, turn valve 3 to admit sample from vacuum lock to sample loading arm, 1. Close valve to vacuum lock. The small amount of gas admitted will not interfere, and will be removed rapidly to the pump. When hydrogen in steel is desired, the samples are injected best through such a lock.

Use of Stopcocks to Provide a Vacuum Lock—An alternative means of admitting samples is shown in Fig. 36-6. The sample is admitted to the lock through the joint, and is manipulated in the glass boat. This lock is evacuated as described above, in 'Injection of Metal Samples into a Vacuum Station,' p. 1567. Then

<sup>30</sup> Manufactured by Jamesbury Corp., Worcester, Mass., vacuum lock developed by National Research Corp.

open  $S_1$ , and push the sample through the hole in the hollow plug by applying a magnet to the glass-enclosed iron slug. The glass boat prevents grease from contaminating the sample. With the use of a magnet, the boat is rotated to drop the sample. After the sample has dropped to the sidearm, close  $S_1$ .

**Fusion Bath Technique.**—Many metals can be analyzed by fusing directly in a graphite crucible, referred to as a dry bath or dry crucible technique. In numerous cases, it is necessary to inject the sample into a bath of another metal. This technique is used when the sample during fusion runs through the graphite crucible, the melting point is too high for satisfactory fusion, or as a possible approach towards minimizing the effect of gettering by evaporated metal films within the furnace. The selection of the most suitable bath for the work, and the technique of application might be described as the art in vacuum fusion. No doubt, there are many alloy combinations that may prove to be satisfactory.

The proportion of sample to bath material can be estimated by studying the phase diagram of the resulting alloy. For best results, the alloy should be liquid at 1900°C. or below, and sufficiently fluid to allow rapid solution of the carbon. Low and erratic recoveries of gas from a sample can often be attributed to a bath that is too viscous.<sup>31</sup> Also, it has been found that when a bath is heated at a fusion temperature, it becomes less fluid to a point where gas bubbles are trapped in the melt. This phenomenon has been found to be due to the carbon continually dissolving and reacting with the bath material. In addition, the temperature of the iron bath must not be allowed to rise above the selected operating temperature either during outgassing of the bath or analysis of the samples. The temperature fluctuation should be avoided because the solubility of the carbon in iron, and many other metals, increases rapidly with an increase in temperature. On a cooling cycle, carbon precipitates out to make a very viscous bath. The high viscosity of the bath traps gas bubbles within the melt and tends to prevent metal samples from alloying properly to give quantitative gas recovery.

Without doubt, iron and platinum are the two elements most widely used and accepted for bath materials.

In addition, tin is often added to the bath along with a sample, to keep fluidity and assist in the alloying of the sample. Also, the tin has a very high vapor pressure at fusion temperature, which acts to stir and blow out the gas in the fusion melt. In the case of high volatile materials known to getter the evolved gas, tin is often added so that it will volatilize to the furnace walls with the getter type material and minimize the gas adsorption. In a fusion where a bath is used along with tin addition, the partial pressure due to the volatile getter material will be lowered.

A bath is used in the following manner: (1) outgas the crucible at 2500°C. for 2 hr.; (2) determine the blank, i.e., the amount of gas evolved at fusion temperature and collection time; (3) inject 25 g. of iron, platinum, or suitable bath material, and outgas for 30 min. Again determine blank and analyze composition; (4) inject samples consecutively, collecting the gas from each and analyzing the composition. Usually, 0.25 g. to 2 g. samples are injected. The sample weight is dependent on gas concentration. In most cases tin is added in an amount equal to about  $\frac{1}{10}$  by weight of the bath. Tin is sometimes added with each sample

<sup>31</sup> Smith, W. H., Vacuum Fusion Analysis by the Iron Bath, *Anal. Chem.*, **27**, 1636, 1955; McDonald, R. S., Fagel, J. E., and Balis, E. W., Vacuum Fusion Analysis of Titanium, Zirconium and Molybdenum, *Anal. Chem.*, **27**, 1632, 1955.

and suitable corrections are applied. This large bath technique is often preferred and found adequate since the technique provides for relatively rapid analysis. The analyst must study his data, however, to determine when the gas recovery is tending to become low due to the solidification of the bath.

Current studies have shown that better recoveries can be obtained especially in metals of low gas concentration by using an intermittent bath.<sup>32</sup> With this method many of the solidification problems are avoided.

An intermittent bath technique is used in the following manner: (1) outgas the crucible at 2500°C for 2 hr; (2) determine the blank, i.e., the amount of gas evolved at fusion temperature and collection time; (3) inject bath (generally 5 g of iron or platinum plus 0.3 g tin); (4) outgas to pump for 30 min and then determine the amount of gas evolved in a fusion period and analyze. This is the blank used for correcting the sample analysis; (5) inject sample keeping the proper ratio of sample to bath, collect gas and analyze. In some cases a known weight of tin is added with the sample and suitable corrections are applied; (6) inject second sample and proceed as described in (5); (7) inject more bath material and repeat procedure for analysis of 2 more samples.

**Flux Technique**<sup>33</sup>—In order to overcome some of the difficulties involved when the fusion bath technique is used, it was found that the sample and the bath or flux material could be injected simultaneously. Platinum is most satisfactory for use as a flux since the oxygen content is low, less than 10 p.p.m., and very uniform. Also the metal has a relatively low vapor pressure which permits fusions at high temperature. The sample to flux ratio should approximate 1 to 10. This method has been found to be applicable to the determination of oxygen in refractory metals. Since no preliminary outgassing of the platinum is required, the analysis time is reduced considerably.

**Tentative Procedure for Preparation of Sample**—The distribution of the oxides, nitrides, and hydrides in most materials is not uniform since in general the greater concentration is near the surface. In view of this, the engineer must consider the preparation of the sample so that the material analyzed is the same as the material used in application.

**Rod or Ingot Material**—Samples in chunk form are preferred in order to keep the surface small relative to the weight of the sample. Prepare the sample by cutting it into small chunks by means of a hacksaw. File the surface on all sides to remove surface scale or oxide and degrease in a solvent. To load into the sidearm of the furnace, handle the sample with tweezers only.

**Sheet, Wire, Tubing**—Cut the material to suitable weight and form so that the material can be injected through the tube of the furnace and into the crucible. Clean the material in solvent to degrease. In some instances when the hydrogen content is immaterial, the samples are treated in an acid etch solution to remove the surface layer of impurity. Generally, the removal of about 0.1 mil from the surface is adequate. In the case of sheet or wire, roll the material into compact form.

**Powder**—In general, metal powder has a high gas content. Weigh small samples (10 to 100 mg) into small tin cups or on a 1 in square of tin foil. Fold and

<sup>32</sup> Beach, A. I., and Guldner, W. G. Symposium on Determination of Gases in Metals, ASTM Special Technical Publication No. 222, 1957.

<sup>33</sup> Hansen, W. R., Mallett, M. W., and Tizciak, M. J. Platinum Flux Technique for Determining Oxygen in Titanium. Anal. Chem. 31, No. 7, 1237, 1959.

compress tin firmly about the powder. Also, pellets can be made by compressing the powder. Avoid washing powder or sponge material in a solvent.

### VACUUM FUSION APPARATUS (FISHER-SERFASS)<sup>34</sup>

A modification of the conventional vacuum fusion system is shown in Fig. 36-30. Since the principle of the method is similar to that described, the details will not be given. The apparatus embodies some features which are advantageous in some

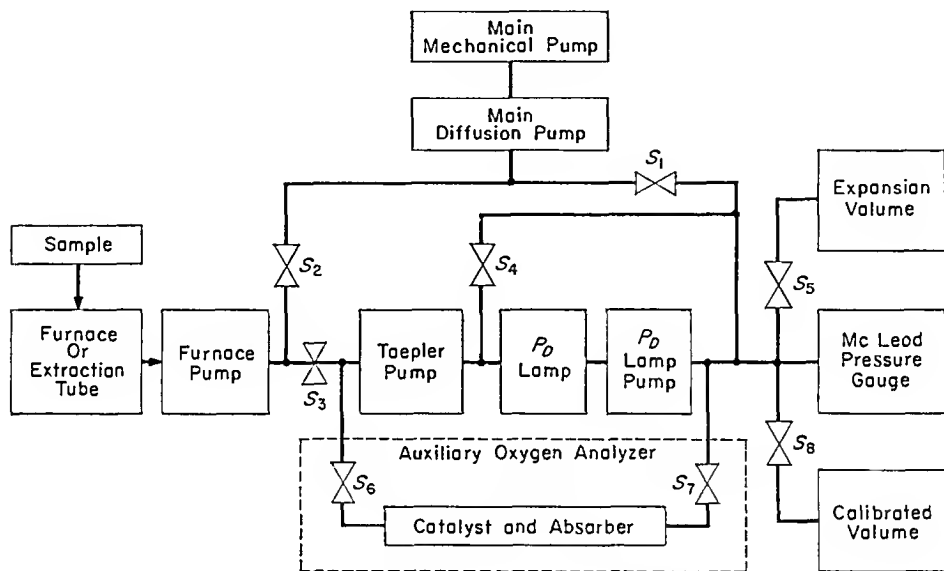


FIG. 36-30. Vacuum Fusion Apparatus (Fisher-Serfass).

fields of work and operation, especially control analysis. The apparatus is unitized and semi-portable.

**Apparatus. Stopcocks.**—To obtain maximum ruggedness, stopcocks have been used instead of mercury cutoffs. Good vacuums can be obtained by using precision ground stopcocks and greasing with care. When an apparatus is under vacuum, and a break occurs in the glass, less damage occurs to the glass in a stopcock type of system.

**Palladium Lamp.**—To remove the hydrogen rapidly during a gas analysis, a palladium lamp or valve is used. This lamp is a hydrogen diffuser, which consists of a thin-walled tube of a palladium-silver alloy, which is bent in the form of a hairpin and mounted within a glass envelope.

Connections are made to the palladium tube by means of glass-to-metal seals. The tube is heated conductively by a low voltage high current power supply.

**Combined Hot Extraction and Vacuum Fusion.**—By means of ball joint connectors, this unit is readily modified for each type of analysis. For example, a vacuum lock is attached in this manner for introducing the sample into the vacuum station to provide for immediate analysis of the sample for hydrogen.

<sup>34</sup> Vacuum fusion apparatus, Fisher-Serfass gas analyzer, available from Fisher Scientific Co.; reproduced with permission from the Milton Roy Co., St. Petersburg, Florida.

**Procedure. Evacuation of the System.**—The system is initially evacuated in the following manner: close stopcocks  $S_3$ ,  $S_4$ ,  $S_7$ , and  $S_8$ , leave all the other valves open, and rotate the manometer to a horizontal position to permit complete evacuation; start mechanical pump, slowly open  $S_3$  to the pump until the pressure is less than 0.1 mm., and then turn on diffusion pumps  $DP_1$  and  $DP_2$ . Evacuate system to a pressure of  $1 \mu$  (.001 mm.) or less, as indicated by the Lippincott-type manometer (sensitivity range 1 to 1000  $\mu$ ); turn heater to outgas the quartz furnace, adjust the temperature to about 800°C., turn on power to heat the palladium filter conduc-

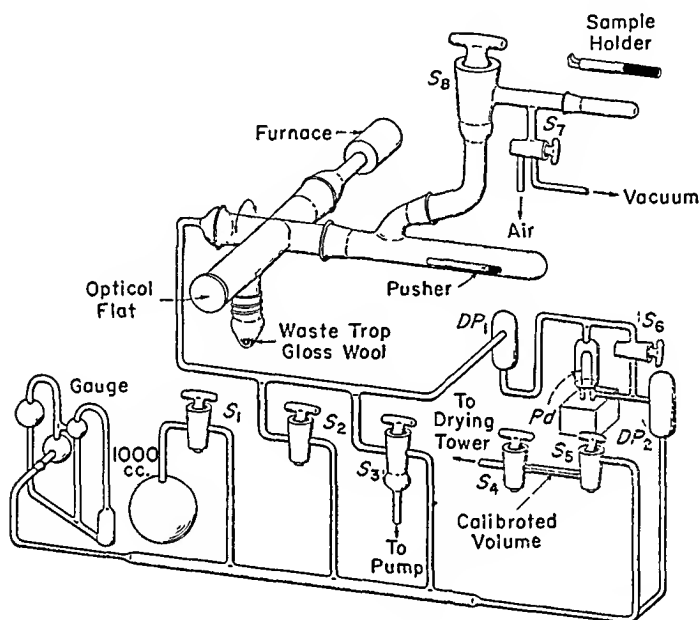


FIG. 36-31. Fisher-Serfass Hydrogen Analyzer.

tively. After conditioning the furnace and system, the volumes of the analytical section must be calibrated. Turn off power to palladium filter, and close  $S_6$ ,  $S_1$ ,  $S_2$ ,  $S_7$ , and  $S_3$ .

**Calibration.**—A known amount of dry air is admitted into a small calibrated capillary volume, and then expanded into the larger unknown volume. In this apparatus, the capillary volume has been previously calibrated by weighing the volume of mercury required to fill the space between  $S_4$  and  $S_5$  (approximately 0.2 cc.). Open  $S_4$  to permit dry air to be admitted from the atmosphere, through a drying tower, into the capillary volume. Close  $S_4$ , open  $S_5$ , and measure the pressure in the unknown volume,  $V_1$ , by means of the manometer. At a temperature,  $T$ , the volume may be calculated from the following relationship:

$$P_0 \times V_0 = P_1 \times V_1$$

where  $P_0$  = atmospheric pressure, in millimeters,

$V_0$  = capillary volume, 0.2 cc.,

$P_1$  = pressure in millimeters in  $V_1$ , and

$V_1$  = volume desired.

where  $P$  = pressure of hydrogen in millimeters, and  $V_1$  or  $V_1 + V_2$  = volumes in cubic centimeters. If the hydrogen is expanded to  $V_2$ , then  $V_1 + V_2$  must be substituted for  $V_1$  in the above relationship. Also, when the pressure is measured at some temperature other than  $25^\circ\text{C}.$ , the value should be multiplied by the ratio of absolute temperatures  $T/T_1$ , where  $T$  is  $273 + 25$  and  $T_1$  is  $273 + t$ .

With this apparatus, a sample can be analyzed for hydrogen in about 15 min. with a precision of 0.2 p. m.

#### LABORATORY EQUIPMENT COMPANY METHOD

In Fig. 36-32 a design of hydrogen extraction apparatus,<sup>35</sup> which is commercially available, is shown.

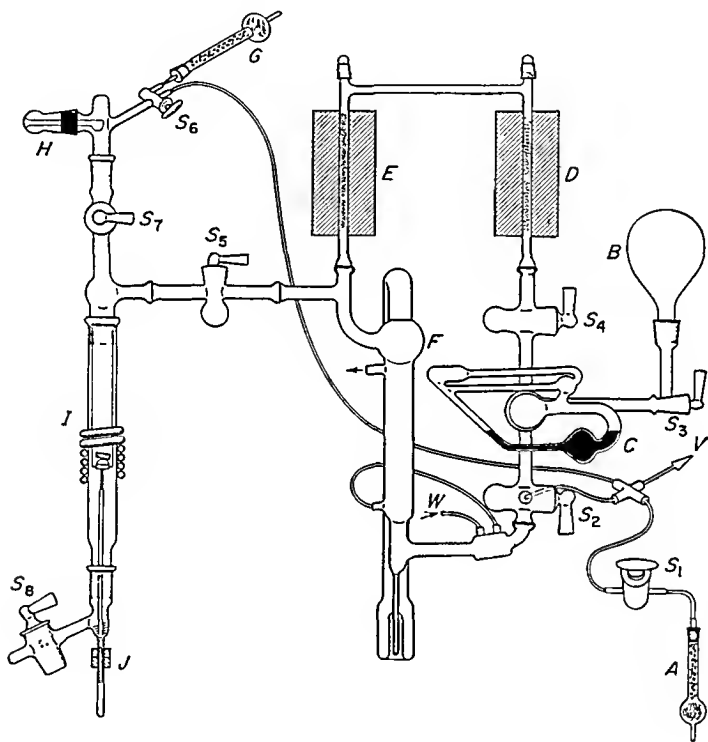


FIG. 36-32. Hydrogen Extraction Apparatus: *A* and *G*, Drying Tubes; *B*, Expansion Bulb; *C*, Pressure Gauge; *D*, Copper Oxide-Misch Metal,  $320^\circ\text{C}.$ ; *E*, Magnesium Perchlorate; *F*, Mercury Diffusion Pump; *H*, Sample Loading Tube; *I*, Induction Furnace; *J*, Solenoid; *W*, Water;  $S_1$  to  $S_8$ , Stopcocks.

**Principle of the Method.**—The principle of the method is based on the extraction of the hydrogen by diffusion from a metal sample, by heating in vacuum. In this apparatus, the sample is heated indirectly by induction in an evacuated system, and, due to the combination of heat and vacuum, the hydrogen is quantitatively evolved. The initial pressure,  $P_1$ , in the vacuum station is practically

<sup>35</sup> Hydrogen analyzer, by Laboratory Equipment Co., St. Joseph, Michigan; reproduced with permission from Laboratory Equipment Co.

negligible but after the extraction the pressure  $P_2$  is readily measured in a known volume with a McLeod gauge

Some materials give up hydrogen only and in this case a simple measurement of  $P - P_1$  is sufficient. Other materials give up carbon monoxide and nitrogen in addition which contribute to the total pressure. In these cases the total gas is passed through an analysis section of the apparatus to remove the hydrogen. The residual gas pressure  $P_4$  is measured. The difference in pressure  $P - P_4$  gives the pressure attributable to the hydrogen only.

**Apparatus** The system is evacuated with a mechanical pump when the handle of  $S$  is in a vertical position. After evacuation of the apparatus the pump is cut off from the station by rotating the handle to a 9 o'clock position. In this position the mercury diffusion pump collects and circulates the gas in the system.

The quartz reaction tube contains a bottomless graphite crucible which is sealed within an evacuated quartz envelope. This crucible has a ceramic and movable bottom. The bottom can be pulled downward by the solenoid  $J$  to drop the sample. The sample drops into the bore of  $S_8$  in which the glass plug is bored partly through. By rotating the stopcock to air the sample is ejected from the analytical station.

The next sample is admitted to the vacuum station through the vacuum lock  $H$ . By closing  $S_7$  and opening  $S_6$  to dry air this section is then adjusted to atmospheric pressure. Remove the tapered joint  $H$ . On removal of the joint the weighed sample is placed in the boat and the joint is replaced. This section is evacuated through  $S_6$ . After evacuation  $S_6$  is closed  $S_7$  is opened and the ground joint  $H$  is rotated to drop the sample out of the holder and into the furnace. The stopcock  $S$  which contains a recessed metal insert to prevent contamination of the sample with grease is then closed.

The tube  $E$  contains magnesium perchlorate and  $D$  a special copper oxide Misch metal type reagent.

The pressure is measured in a calibrated volume by means of the rotating type of McLeod gauge  $C$ . If the pressure is too high for the gauge the gas is expanded to the volume  $B$ .

**Procedure**—Evacuate the system with the mechanical pump by opening  $S$  (handle in vertical position). Turn on diffusion pump  $F$  and bake out ovens  $E$  and  $D$ . Initially condition the system for several hours turn off heater  $E$  and close  $S$  by rotating handle to 9 o'clock. Test to determine if apparatus will hold the vacuum by periodically measuring the pressure with the McLeod gauge.

Calibration of the apparatus is accomplished by admitting dry air into the system with a dosing stopcock attached at  $H$ . The plug of a dosing stopcock is bored partly through so that when the stopcock is turned to atmosphere the bore will fill with air that has passed through a drying tower and is at atmospheric pressure. Since the volume  $V_1$  of gas and the pressure  $P_A$  (atmospheric pressure) is known a known quantity of gas is admitted by rotating the stopcock to the system. With  $S_4$  and  $S_3$  closed open  $S_7$  to permit the gas to be collected by the diffusion pump and in the small volume  $V_T$ . Measure the pressure  $P_T$ . The volume of  $V_1$  at room temperature is calculated from the following equation

$$V_T = \frac{P_A V_1}{P_T}$$

where the pressure is measured in millimeters of mercury and the volume in cubic centimeters. Suitable corrections must be applied if the temperature of the room

is not controlled. In like manner, the total volume plus volume  $B$  may be calibrated by opening  $S_3$ .

A blank determination is made after the system has been well outgassed. The graphite crucible, which is enclosed in quartz, is heated to  $1200^{\circ}\text{C}$ . or lower for some metals, for the same length of time (4 min. or more) as for the sample. The gas is collected in  $V_T$  and the pressure  $P$  is measured. The gas is analyzed by opening  $S_4$  ( $S_5$  can be left open if the pressure is low) to circulate the gas over the copper oxide and magnesium perchlorate. After 4 min., close  $S_4$  to collect the gas in  $V_T$ , and measure the pressure  $P_2$ . The pressure due to the hydrogen is  $P - P_2$ .

The extraction time and temperature are determined by analyzing a series of a sample where the extraction time and separation time are kept at 4 min. each, and the temperature is varied. In this way, the optimum temperature for the extraction is determined.

The analysis of a sample is carried out in the same manner as the blank. With  $S_7$  closed, dry air is admitted through  $S_6$ . The sample holder,  $H$ , is removed and the sample is placed in the boat. After replacing  $H$ ,  $S_6$  is opened to pump for evacuation. Then, close  $S_6$ , open  $S_7$ , and rotate  $H$ , to drop the sample. Close  $S_7$ . For collection of gas,  $S_4$  is closed, and  $S_2$  is opened to calibrated volume. The amount of hydrogen is measured and analyzed as described above for the blank. This value must be corrected for the blank. The percentage of hydrogen is calculated in the following manner:

$$P_{(\text{mm.})} \times V_{(\text{cc.})} = \text{hydrogen}_{(\text{ml.})}$$

$$\text{Weight percentage of hydrogen at } 25^{\circ}\text{C.} = \frac{\text{milliliters of hydrogen} \times 0.108 \times 1000}{\text{weight of sample (micrograms)}}$$

If the gas is measured at some temperature other than  $25^{\circ}\text{C}$ ., suitable corrections must be applied.

The sample is prepared by cutting with a hacksaw, or shearing, or in a manner to minimize heating and contamination of the sample. Cut a sample from chunk material that will fit into the boat, and is capable of passing through  $S_7$ . The normal sample size is 0.2 to 0.5 g. File or sand off any heavy oxide coating, and degrease in trichloroethylene, followed by a rinsing in acetone. Weigh and insert into the holder,  $H$ , for analysis.

## DETERMINATION OF OXYGEN IN METALS BY INERT GAS FUSION

Inert gas fusion provides a unique approach for a rapid, single, and inexpensive method for determining oxygen in metals. It is generally used as a control tool for analyzing metals of relatively high oxygen levels, 100 to 2000 p. p. m. With modifications in technique and apparatus, this method can be applied to samples containing in the range of a few parts per million of oxygen, to oxides of metals containing several per cent. Three alternatives have been developed that give adequate results when compared to vacuum fusion.



**Preparation of Crucible.**—The graphite crucible,  $M''$ , is preheated in a muffle furnace at  $1000^{\circ}\text{C}$ . for 15 min., and followed by a vacuum induction heating at  $1000^{\circ}\text{C}$ . in a rough vacuum, less than 0.1 mm. for 1 hr. After the crucible temperature drops to ambient, add 15 g. of tin, and heat in nitrogen to  $1250^{\circ}\text{C}$ . for 15 min. In this manner, several crucibles containing the tin bath are prepared ahead of time and stored in a desiccator. Determine the blank, which is the amount of carbon dioxide adsorbed in the Schwartz absorption tube.  $R$ , during 15 min. of heating at  $1250^{\circ}\text{C}$ . of the preconditioned crucible and tin. Allow the crucible to cool to ambient, place the sample in the crucible, and repeat the above procedure. Weigh the carbon dioxide collected.

$$\text{Oxygen in sample, per cent} = .364 \frac{(W_3 - W_2) - W_1}{\text{weight (grams) of sample}} \times 100$$

where  $W_1$  = weight of carbon dioxide in grams, blank,

$W_2$  = weight of absorption tube in grams, and

$W_3$  = weight of absorption after fusing sample, in grams.

#### APPLICATION OF THE CAPILLARY TRAP METHOD TO INERT FUSION IN ARGON

A modification of this technique,<sup>38</sup> which attached a real significance to inert fusion by increasing the sensitivity, is shown in Fig. 36-34. This apparatus consists of a clear quartz fusion furnace, Fig. 36-35, within which a graphite crucible is supported by a tungsten rod. The crucible is heated in argon by high-frequency induction. The carbon monoxide formed during fusion is oxidized to carbon dioxide by a modified form of Schütz's reagent,<sup>39</sup> which provides an indicating reagent operating at ambient temperature. In addition, the apparatus consists of a capillary trap (Fig. 36-36),  $T$ , in Fig. 36-34, which provides for the measurement of the carbon dioxide gas in a small volume to achieve adequate sensitivity. In this apparatus, the vacuum pump is used to evacuate the capillary only.

**Procedure.**—Insert the sample at  $D$ , and replace the glass plug; no grease or wax is required. Adjust the argon flow with valve  $V_1$  until gas bubbles out slowly through the manostat. Turn on the vacuum pump, close  $V_5$ , and open valve  $V_6$  slowly, and adjust the mercury column to the zero mark by raising or lowering the beaker. With  $V_3$  and  $V_4$  closed, open  $V_2$  and adjust  $V_5$  to give a manometer reading of 50 mm., which corresponds to an argon flow of about 100 cc. per min. Turn on cooling water to the furnace jacket, and heat the crucible and bath material by induction to  $1800^{\circ}\text{C}$ . for 20 min. Then, open  $V_3$  and  $V_4$ , and close  $V_2$ , which directs the flow of argon through the oxidizing reagent,  $R$ .

Determine the blank by placing a Dewar flask containing liquid nitrogen about trap,  $T$ . After 10 min. of heating, close  $V_5$ , and evacuate the argon in the trap. Close  $V_6$ , and remove the Dewar flask, warm the trap with a water bath, and allow the trap to come to ambient temperature. Read the pressure to the nearest 0.5 mm. Repeat blanks until a satisfactory level is obtained; the blanks should be equivalent to 2 to 7  $\mu\text{g}$ . of oxygen. Flush out carbon dioxide.

**Analysis of Sample.**—Replace Dewar flask about trap,  $T$ . Inject the sample into the crucible by raising the iron-cored plunger by means of a solenoid. Repeat the procedure as described under blank determination, and read the manometer pres-

<sup>38</sup> Smiley, W. G., *Nuclear Sci. Abstr.*, **3**, 391, 1949; Determination of Oxygen in Metals Without High Vacuum by Capillary Trap Method, *Anal. Chem.*, **27**, 1098-1102, 1955.

<sup>39</sup> Schütz, M., *Ber.*, **77B**, 484, 1944.

sure Shut off induction heater and when the crucible is cool open *D*, and insert the next sample

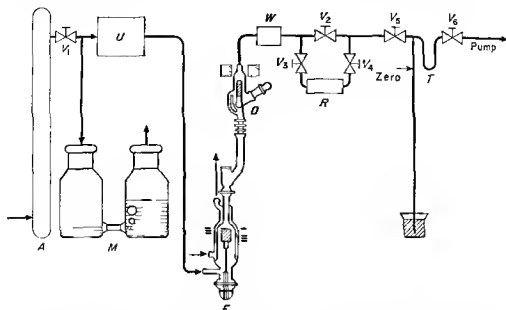


FIG. 36-34 Inert Gas Argon Fusion—Capillary Trap Method. *A* Ascarite and Magnesium Perchlorate; *D* Sample Holder; *F* Induction Furnace; *M* Manostat; *R* Modified Schütz Reagent; *T* Capillary Trap and Manometer; *U* Purification Furnace Containing Uranium. *V*<sub>1</sub>, *V*<sub>2</sub>, *V*<sub>3</sub>, *V*<sub>4</sub>, *V*<sub>5</sub>, *V*<sub>6</sub> Brass Bellows Type Valves; *W* Glass Wool and Magnesium Perchlorate. (Copyright 1955 by The American Chemical Society, reproduced with permission)

**Calibration of Capillary Trap**—Denoting the volume of the capillary trap above the zero mark and between *V*<sub>3</sub> and *V*<sub>6</sub> by *V*, the cross section of the capillary bore by *A*, and the manometer reading by *X*, the weight of oxygen *W* is

$$W = \frac{16X(V + AX)}{RT}$$

The atomic weight of oxygen is used as only 1 atom of oxygen per molecule of carbon dioxide comes from the sample. Expressing the weight in micrograms and linear dimensions in millimeters with an ambient temperature of 25°C

$$W = 0.0086(VX + AX^2) \text{ micrograms,}$$

Then

$$\text{oxygen in sample, per cent} = \frac{1}{10} \frac{W_{\text{sample}} - W_{\text{blank}}}{\text{weight of sample, in milligrams}}$$

#### APPLICATION OF A CONDUCTOMETRIC METHOD TO INERT FUSION IN ARGON<sup>40</sup>

This method, a modification of the 2 previously described techniques embodies a better fusion furnace in conjunction with a conductometric means for measuring the carbon dioxide. The analysis time is about 8 min. Purified argon gas is

<sup>40</sup> Apparatus developed and manufactured by Laboratory Equipment Co., St. Joseph, Michigan, reproduced with permission from the Laboratory Equipment Co.

passed over a hot graphite crucible in which the sample is fused. Oxides in the sample are reduced by the carbon to form carbon monoxide. This gas is converted to carbon dioxide that is then absorbed in dilute caustic. The change in conductivity of the solution is measured in terms of resistance. This apparatus is simple to operate, sensitive, and commercially available. It is most adaptable to

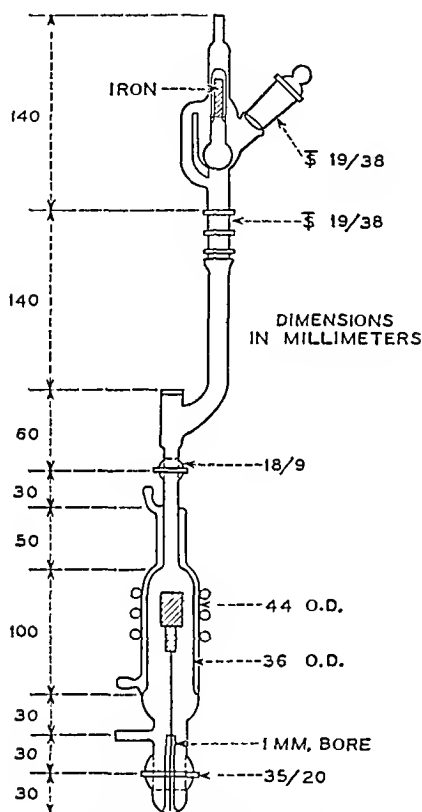


FIG. 36-35. Clear Quartz Fusion Furnace.

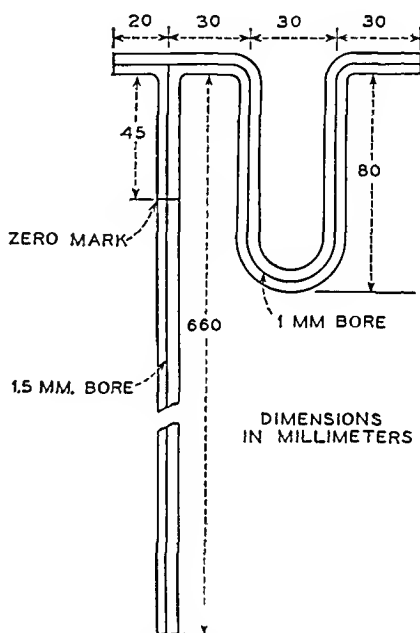


FIG. 36-36. Capillary Trap.

determining oxygen in metals in the range of 50 to 2000 p. p. m. With a reasonable adjustment of sample size, the optimum amount of oxygen can be introduced for analysis. Fusion bath techniques are employed in a manner similar to that described under vacuum fusion.

*Apparatus.*—A schematic diagram of this apparatus is shown in Fig. 36-37.

*Purification of the Argon.*—Argon is admitted to the apparatus by means of a diaphragm 2-stage regulator valve, through a purifying train consisting of copper oxide 300°C., *A*, Ascarite and magnesium perchlorate, *B*, sulfuric acid, magnesium perchlorate, and Ascarite. The gas flow is indicated by a ball-type flow meter, and further regulated by means of the needle valve, *D*. Then, the gas is passed over the hot titanium sponge, *F*, at 600°C. In this flow system, a mercury pressure relief valve, *H*, has been inserted. This purified argon passes into the furnace.

**Furnace Assembly.**—Fill the quartz thimble about  $\frac{1}{2}$  full of carbon black, tap lightly to settle carbon black, and insert the graphite crucible with the top of the crucible about  $\frac{1}{16}$  in above the top of the thimble. Add carbon black until the thimble is full. Lightly tap the thimble to settle the carbon black but avoid packing. Blow out any loose powder that has fallen into the crucible by means of a glass tube. The carbon black must be loose about the crucible to avoid danger of coupling by the high frequency heater and to provide adequate insulation.

Place the crucible assembly on the quartz pedestal and raise the furnace base to the bottom of the quartz tube furnace. In this way the crucible is placed in the high frequency field. A rubber O ring provides an adequate seal between the quartz tube and the furnace base. At the top of the furnace an inner tube serves to tunnel the samples from the loading stopcock into the crucible.

**Conductometric Analyzer.**—This analyzer consists of a sensitive Wheatstone bridge having 2 conductivity dip cells. 1 as a reference, and the other as a measur

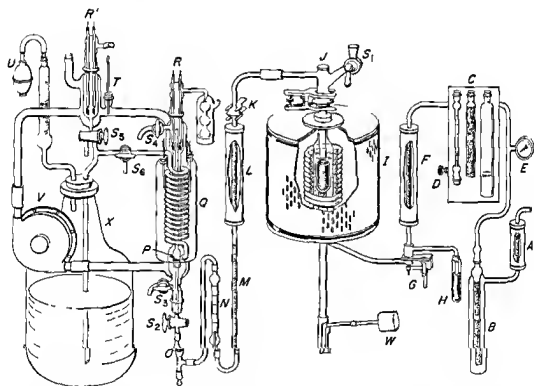
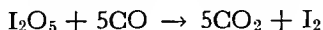


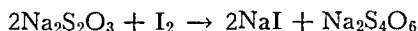
FIG. 36-37. Inert Gas Fusion Apparatus. A, Copper Oxide Furnace; B, Trap, Ascorbic and Magnesium Perchlorate; C, Purifying Train Concentrated Sulfuric Acid, Ascorbic Magnesium Perchlorate, Flow Meter; D, Needle Valve; E, Pressure Gauge; F, Furnace Containing Titanium Sponge at 600°C; G, Quick Disconnect; H, Mercury Pressure Release; I, Induction Furnace Graphite Crucible Flashed in Lamp Black; J, Optical Unit; K, Bill Joint; L, Furnace Containing Iodine Pentoxide (140°C); M, Sodium Thiosulfate Crystals; N, Flow Meter; O, Trap, Porous Frit Covered with Mercury; P, Porous Frit for Dispensing the Gas in the Barium Hydroxide; Q, Water Jacket Containing Temperature Regulator and Heater; R, Conductivity Cell, Measuring; R', Conductivity Cell, Reference; S1, Sample Loading Stopcocks; S2, 3, 4, 2 Way Stopcocks; S5, 5, 3 Way Stopcocks; T, Thermomuter; U, Rubber Squeeze Bulb; V, Water Circulator; W, Counterweight; X, Carbonyl Barium Hydroxide.

ing cell in the sorption solution. Both cells dip into a dilute barium hydroxide solution and are balanced in the bridge circuit. The argon gas containing the carbon dioxide bubbles through a mercury trap and a glass diffusion frit into the barium hydroxide contained in the measuring cell. The resistance required to rebalance the bridge is used as a measure of the carbon dioxide absorbed. Since the conductivity of a solution changes with temperature, the cells and analyzer are water-jacked with thermostatic control at some temperature higher than room temperature (40°C.).

**Reagents.** Iodine Pentoxide.—Specially prepared iodine pentoxide is used at about 140°C. to oxidize the carbon monoxide evolved from the fusion of the sample



**Sodium Thiosulfate.**—The resulting iodine is absorbed by sodium thiosulfate



The carbon dioxide is then carried by the argon into the measuring cell containing the barium hydroxide. The change in conductivity of the solution is measured in ohms.

**Barium Hydroxide.**—The barium hydroxide is prepared as follows: (1) pass tank nitrogen through 17 l. of distilled water contained in an 18-l. flask for 45 min. (For best results use distilled water that has been passed through a cation and anion exchange resin, e.g., Amberlite MBI or equivalent); (2) boil about 1 liter of distilled water for a few minutes to render it free from carbon dioxide. Add 15 g. of barium hydroxide to a portion of the water, and vacuum filter it through a fine glass frit containing some paper pulp. Add this solution to the 17 l. of distilled water, and adjust volume to 18 l.; (3) stopper, shake, and allow to settle for about 1 week before using. In a similar manner, a solution containing as low as 5 g. of barium hydroxide in 18 l. is prepared when the amount of oxygen to be measured is very low, 10 to 100 p. p. m.

**Procedure.** Conditioning the Crucible.

1. Turn on argon and flush system.
2. Turn on catalyst heaters, thermoregulator heater for water bath, filaments in the induction heater, water supply, and allow time to reach equilibrium.
3. Adjust argon flow to 0.5 l. per min. with needle valve when the sample loading stopcock,  $S_1$ , is open to atmosphere.
4. Turn on induction heater and raise the temperature of the crucible slowly until the crucible is at least 2500°C. The temperature is measured through the optical flat,  $J$ , at the top of the furnace, by means of an optical pyrometer. Continue heating for 15 min.
5. Lower the temperature of the crucible to fusion temperature, 1650° to 2000°C., depending on the metal to be analyzed.
6. Check the blank by closing stopcock,  $S_1$ , and allowing the argon to pass from the furnace over the iodine pentoxide and sodium thiosulfate.
7. Fill the measuring cell,  $R$ , by applying a pressure with the squeeze bulb over the barium hydroxide solution, close  $S_3$  and  $S_4$ , and open  $S_6$  to permit the solution to flow into the cell to a point above  $S_4$ . Turn off  $S_6$  and  $S_2$ , and open  $S_4$  to drain, in order to adjust the solution to a constant volume. Open  $S_2$  fully, adjust argon flow with the needle valve to 200 to 300 ml. per min., as indicated by the flow meter on the conductometric unit.

- 8 Fill the reference cell *R* by opening *S*<sub>2</sub> to permit the barium hydroxide to rise about 1 in above the electrodes, and about ½ in below the water level. Flush several times when a new solution of barium hydroxide is used. The cell is drained by opening *S*<sub>1</sub> to drain and removing the rubber policeman on the cell to let in air. The barium hydroxide in this cell is replaced only when a new solution is used, or when a balance on the bridge cannot be obtained.
- 9 Balance the bridge by superimposing the lines on the cathode ray tube. Collect gas from the hot crucible for 3 min, turn off plate current, and continue the argon flow for another 5 min. Balance the bridge and record the ohms resistance required to bring the lines into coincidence. If the resistance change is reproducible and of the order of 2 ohms or less, the apparatus can be standardized (solution containing 15 g per 18 l).

**Standardization Use of Silver Oxide**—The method is standardized with weighed amounts of silver oxide that contain 6.9% oxygen. In this manner, a calibration curve is established on graph paper with the oxygen content plotted versus the resistance.

- 1 Weigh approximately 2, 3, and 4 mg of silver oxide into tin cups (manufactured by Laboratory Equipment Co., volume slightly less than 0.2 cc), 1.5 cm high, 0.5 cm in diameter, and weighing about 0.14 g. Flatten cups with spatula, and roll with tweezers into a compact sample. Sheet tin foil may be used also.
- 2 Place standard sample in the loading stopcock, allowing the argon to pass over the sample and out to the atmosphere during the time required to raise the crucible from ambient to operating temperature (5 min).
- 3 Repeat procedure as outlined under blank and inject sample.

**Use of Potassium Acid Phthalate**—Because the weighing of milligram amounts of silver oxide is both tedious and time consuming, potassium acid phthalate<sup>41</sup> can be used to great advantage. By making a standard solution and dispensing known amounts into the tin cups by means of a micro syringe, it is possible to prepare approximately 100 standards in 30 min.

**Preparation of Solution**—Dissolve 6.38 g of NBS potassium acid phthalate, which contains 31.34% oxygen (previously oven dried at 115°C), in distilled water and dilute to 1 liter. One  $\lambda$  (0.001 ml) of solution contains potassium acid phthalate equivalent to 2  $\mu$ g of oxygen.

**Dispensing of Solution**—Use a micro syringe, with a 100  $\lambda$  capacity, which is calibrated to an accuracy of  $\pm 1 \lambda$  (Syringe manufactured by Hamilton Co., Whittier, California, #5710N, and may be obtained with a Chaney adapter S710NCH or micro buret syringe, sold by Scientific Glass Apparatus Co., Bloomfield, New Jersey). Dispense solution into tin cups, and dry in an oven at 100°C or below. Flatten out tin cups with a spatula, and roll into a compact sample with tweezers. In this way, standards can be readily prepared in the range of 50 to 400  $\mu$ g of oxygen. By making up standard solutions of various concentrations, standards may be prepared in like manner from 10 to 2000  $\mu$ g.

The blank due to the tin is generally built into the calibration curve. The error

<sup>41</sup> Technique suggested by T. D. McKinley and associates at E. I. DuPont de Nemours, Wilmington, Delaware.

is automatically subtracted by using an equal amount of tin in the fusion of the sample. The total time schedule is adjusted according to the type and quality of the measurements desired. A recommended time schedule to obtain maximum precision is as follows:

To raise the furnace from ambient to fusion temperature	5 min.
To fill the conductometric cell and make necessary adjustments, about	2 min.
To provide adequate fusion, heat sample for	3 min.
To sweep all carbon dioxide into sorption cell, an additional	5 min.
Total analysis time	15 min.

**Analysis of Sample.**—Adjust sample size so that the oxygen present will not be greater than 400  $\mu\text{g}$ . Prepare samples in a manner similar to that described under vacuum fusion. Use a tin cup and fusion baths when required. Run sample for the same time and temperature as the blank. Measure resistance change and determine oxygen content from the calibration chart.

Since the calibration curve can be extended to 2000  $\mu\text{g}$ ., a sample containing large amounts of oxygen may be analyzed. There is a slight curvature to this extended calibration curve, but any 400- $\mu\text{g}$ . portion can be assumed to be a straight line. When the oxygen content is not known, run the sample first, and then follow with standards that contain oxygen contents just above and below that of the sample.

When weaker solutions of barium hydroxide are used, low oxygen standards are used, i.e., when 5 g. of barium hydroxide are used in 18 l., the maximum oxygen that can be measured is about 250  $\mu\text{g}$ . This solution is very suitable down to 10  $\mu\text{g}$ . of oxygen.

When larger amounts of oxygen are to be measured, such as are found in the reduction of metal oxides, the carbon dioxide is measured best by means of an adsorption tube containing Ascarite, attached at the end of the tube, *M* (Fig. 36-37).

## DETERMINATION OF CARBON IN METALS

The change in the carbon content of a metal, as a result of processing, is often as important as the measurement of the oxygen content. The carbon-oxygen ratio has been found to change with processing, and is of prime importance in many gas phase studies.

Most methods for determining carbon depend on burning the metal sample in oxygen, and measuring the amount of carbon dioxide. The measurement of the carbon dioxide is made in several ways: volumetric analysis by absorption in potassium hydroxide; gravimetric analysis by absorption in Ascarite or similar solid reagent; low pressure analysis by separation by fractional freezing, and then measuring the carbon dioxide in a known volume by means of a McLeod gauge; and conductometric method by absorption of the carbon dioxide in dilute barium hydroxide, and measuring the change in conductivity.

The low pressure combustion method for determining small amounts of carbon and the conductometric analyzer are described below.

*DETERMINATION OF CARBON IN METALS BY THE LOW PRESSURE COMBUSTION METHOD*<sup>42</sup>

**Principle of the Method** The principle of this method is based on the combustion of the metal sample in a reduced pressure of oxygen during which the carbon is converted to carbon dioxide. The carbon dioxide is frozen out in a liquid nitrogen trap, the excess oxygen is pumped out, and the liquid nitrogen is removed from the trap to allow the carbon dioxide to warm up to ambient temperature. The carbon dioxide gas is measured in a known volume by means of a McLeod gauge.

This method has found wide application in the determination of carbon in high purity metals where the carbon content is often less than 0.01%. With an expansion volume or by aliquoting the range can be extended to cover samples containing carbon as high as 0.1%. Since the precision of the method has been established on the order of 0.0002% carbon based on the analysis of 0.5 g. NBS samples, the technique can be applied to the determination of carbon in small samples. While the method was developed for application to steel, it can be applied to most other metals.

**Apparatus and Reagents** The low pressure combustion apparatus is shown in Fig. 36.38. It consists essentially of a purification train, a combustion chamber, and an analysis system. This apparatus is evacuated by means of a single stage mercury diffusion pump which is backed by a mechanical pump (Cenco Hypervac No. 2) or its equivalent. Also, a small auxiliary pump (Cenco Hyvac or its equivalent) for a backing vacuum is required.

**Purification of Oxygen** The oxygen is admitted from a tank connected at *A* to a standard 2 stage regulator through flexible copper tubing to the glass apparatus. A copper-to-glass seal is used to make the connection. The oxygen is admitted to the evacuated system through the stopcock *S*<sub>1</sub> through the liquid nitrogen trap over the palladium catalyst (400°C.) and then through another double liquid nitrogen trap. The palladium catalyst is contained in a clear quartz tube that is stop sealed to the glass apparatus at each end. The oxygen is purified by condensing approximately 10 ml. in trap *T*<sub>1</sub> and then evaporating a portion of this and recondensing it in traps *T*<sub>2</sub> and *T*<sub>3</sub>. These traps collect any oxidation products formed by passing the oxygen over the catalyst and hold an ample supply of liquid oxygen until ready to be admitted to the combustion furnace.

At liquid nitrogen temperature the vapor pressure of oxygen is approximately 16 cm. so that it is possible by raising the mercury in cutoff *I* to hold a supply of pure oxygen in traps *T*<sub>2</sub> and *T*<sub>3</sub> while evacuating and outgassing the analysis and combustion sections. The capillary by pass (1 mm. bore) in *I* is a device for admitting oxygen at a relative high pressure of about 16 cm. to an evacuated system. The capillary *K* serves a similar purpose in exhausting the excess oxygen slowly subsequent to the combustion of the sample.

**Combustion Furnace**—The combustion furnace is sealed on at *D* and consists of a tubular chamber made of Pyrex in which is suspended coaxially a platinum crucible (Baker Platinum Co. Bell Telephone Laboratory Special) with reinforced rim which contains the refractory oxide crucible (Coors AL200 high alumina or equivalent). An outer ceramic crucible supports the above assembly. Fig. 36.39 and

<sup>42</sup> Wooten, I. A. and Guldner, W. C. Determination of Carbon in Low Carbon Iron and Steel. *Ind. Eng. Chem. Anal. Ed.* **14**, 833-8 (1942) copyright 1942 by the American Chemical Society reproduced with permission.



acts as a heat radiation shield. Platinum wire .050 in. is hooked through an eye of a glass support, with the ends hooked through holes located diametrically opposite in the outer ceramic crucible. The length of the loop is adjusted to hold the crucible just below the sample chute. The sample is prepared in the form of fine turnings, drillings, nibblings, or thin chips, and is introduced into the side-arm, *Q*, and sealed off. As many as 20 samples have been loaded in respective side-arms and held for analysis. The advantage of this technique is that it permits the loading of all the samples at one time to eliminate the danger of changing the furnace blank. Also, it is possible to run a blank on the crucible prior to an analysis.

The platinum crucible is heated by high frequency induction (500 kc.-2 kw. output), which serves as the heating or conducting element to the ceramic crucible.

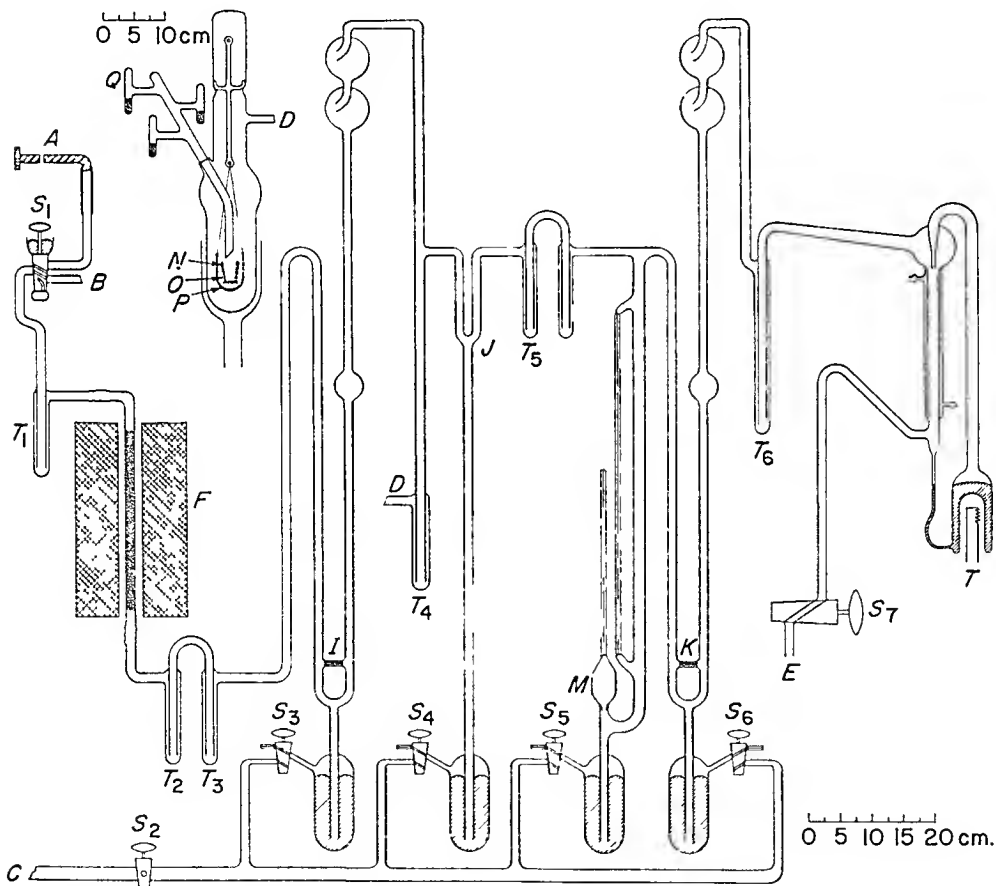


FIG. 36-38. Low Pressure Combustion Apparatus for the Determination of Carbon: *A*, Flexible Copper Tube with Copper-to-Glass Seal; *B*, *C*, Outlet to Rough Backing Vacuum; *D*, Connection to Analysis System; *E*, Outlet to Mechanical Oil Pump, Cenco Megavac; *F*, Electric Furnace; *G*, Palladium Catalyst on Alumina; *H*, Clear Quartz Tube; *I*, *J*, and *K*, Mercury Cutoffs; *M*, McLeod Gauge; *N*, Alumina Crucible, Coors; *O*, Platinum Crucible with Reinforced Rim; *P*, Alumina Crucible, Coors; *Q*, Side Tube for Admitting and Storing Samples; *S*<sub>1</sub> to *S*<sub>7</sub>, Stopcocks; *T*, Resistance Heater; *T*<sub>1</sub> to *T*<sub>6</sub>, Traps.

For the combustion of metals difficult to burn, a 60/40 platinum rhodium crucible has been used to prevent excessive damage to platinum crucibles.

**Calibration of Apparatus**—The volume between the cutoffs *J* and *K*, in which the carbon dioxide is measured is calibrated by admitting the maximum amount of purified dry oxygen that can be measured by the gauge (McLeod gauge bulb volume 120 cc, pressure range 0.00002 to 0.7 mm) Record the pressure, and, with

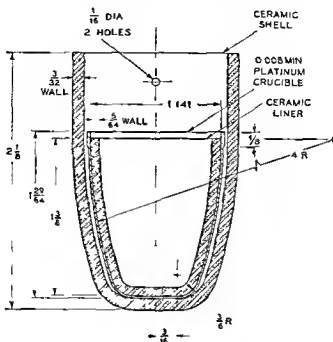


FIG. 36-39 Crucible Assembly (All Dimensions in inches)

the gas trapped in the bulb open the cutoff *A*, to the pump to remove all of the gas external to the bulb. Raise cutoffs *J* and *K* to the calibration lines. Lower the mercury in the McLeod gauge below the point of cutoff to permit the gas to expand into the volume between the cutoffs. Remeasure the pressure.

Calculate the volume from the following relationship

$$V_x = \frac{P_1 \times V_1}{P_x}$$

where  $V_x$  = total volume between cutoffs *J* and *K*,

$P_x$  = pressure between cutoffs *J* and *K*,

$V_1$  = volume of gauge, in cubic centimeters, and

$P_1$  = initial pressure of oxygen in the gauge

The gauge may be used in a similar manner, to aliquot the gas evolved from a sample when the pressure is too high to measure. By trapping an aliquot in the bulb the gas external of the gauge is pumped out. The gas in the bulb is then expanded in the volume between cutoffs *J* and *K*, and the pressure is measured. The amount of gas measured in the aliquot is multiplied by the ratio of the volume  $V_1$  to the total volume  $V_x$ .

*Procedure.*—Weigh 0.5 g. of the degreased sample. With a gas-oxygen torch, heat the top of the sidearm, *Q*, and blow out the end, taking care that glass flake does not fall inward. Insert sample and reseal. In like manner, samples are inserted in the remaining sidearms.

Those metals that are nonmagnetic are loaded into magnetic boats and used in a horizontal tree, such as that described above, under "Injection of Metal Samples into a Vacuum System," p. 1567.

Some metals, such as high melting and high purity alloys, are difficult to burn. In these cases, where poor combustion is observed, weigh a 0.5 g. portion of NBS No. 131 silicon steel, and insert it with the sample as a flux. The heat evolved in burning the flux raises the temperature sufficiently above the temperature of the crucible, to burn the sample. Some investigators include a small amount of tin.

Close stopcocks  $S_1$ ,  $S_2$ , and  $S_7$ , and turn stopcocks  $S_3$ ,  $S_4$ ,  $S_5$ , and  $S_6$  to connect the mercury wells to the back vacuum in the manifold. Turn on both mechanical pumps, and slowly open  $S_7$  until the mercury begins to rise in the tubes. Counteract this rise by opening  $S_2$  to the mechanical pump attached at *C*, thus keeping the mercury below levels of cutoff. After the system has been evacuated, close  $S_3$ ,  $S_4$ ,  $S_5$ , and  $S_6$ . Turn on the heater for the diffusion pump, and adjust the heater voltage to provide a rapid stream of mercury through the jet. Turn on the catalyst furnace, *F*, and raise the temperature to about 1100°C. Evacuate the entire system for at least 30 min. Then lower the temperature of the catalyst to about 400°C. Raise the mercury in cutoff *I* by opening  $S_3$  to the atmosphere.

Purify the oxygen by placing Dewar flasks containing liquid nitrogen on traps  $T_1$ ,  $T_2$ , and  $T_3$ , and slowly admit oxygen through stopcock  $S_1$ . When the pressure of oxygen exceeds 16 cm. of mercury, as indicated on cutoff *I*, the oxygen will liquify in trap  $T_1$ . After about 10 ml. of oxygen have been formed, close  $S_1$ . Partially lower the Dewar flask from trap  $T_1$  to permit the major portion of the oxygen to distill over the catalyst and recondense in traps  $T_2$  and  $T_3$ . Replace Dewar flask about  $T_1$ , and keep liquid nitrogen in these flasks throughout the day.

Raise the induction coil about the furnace to a point where the top of the coil is about  $\frac{1}{8}$  in. below the top of the platinum crucible. Turn on the heater and increase the power until the temperature of the crucible is 1150° to 1200°C., as measured with an optical pyrometer.

Raise the mercury in the capillary cutoff, *K*, and the McLeod gauge, *M*, by opening  $S_6$  and  $S_5$  to the atmosphere. Open stopcock  $S_4$  to air until the mercury reaches a height just below the cutoff *J*.

Admit purified oxygen by slowly lowering the mercury in cutoff *I*, by turning  $S_3$  to the manifold until the oxygen bubbles through the capillary and into the combustion furnace. Admit oxygen until the pressure is about 16 cm. as indicated on the mercury cutoff *K*. Raise the mercury in *I* by opening  $S_3$  to air. Place a Dewar flask, containing a mixture of dry ice and ethylene glycol monoethyl ether acetate, about trap,  $T_4$ , and liquid nitrogen about  $T_5$ . Heat the crucible to at least 1150°C. for 10 min. Turn off power. Remove the excess oxygen by slowly turning  $S_6$  to the manifold until the mercury is sufficiently low to permit the oxygen to bubble through the capillary to pump. This evacuation should be carried out slowly to eliminate the danger of sweeping sulfur compounds and water from  $T_4$  and carbon dioxide from  $T_5$ . When the pressure is about equal, open cutoff *K* fully to obtain rapid evacuation. Evacuate for 10 min., raise the mercury in cutoffs *J* and *K* to calibrated points of cutoff, and remove the liquid nitrogen from trap  $T_5$ . Allow ample time for the trap to reach ambient temperature, and record the

pressure as measured with the McLeod gauge. The value of the blank should not exceed 0.0002% carbon based on a 0.5 g sample. Evacuate the carbon dioxide and repeat if blank is not satisfactory. If the blank is satisfactory proceed with the analysis of a sample.

To determine the carbon content of a sample proceed as described in determining the blank. Admit the oxygen, turn on the power to heat the crucible to at least 1150°C and inject the sample into the hot crucible. The sample is removed from the sidearm by means of a magnet. In a similar manner the remaining samples are analyzed.

After completing the firing of the samples the excess liquid oxygen must be removed with care. With  $S_2$  open to air, open  $S_1$  to  $B$  which is connected to the backing vacuum pump. Since the vapor pressure of oxygen at liquid nitrogen temperature is about 16 cm, the vacuum pump will remove the excess oxygen. Then it will be safe to remove the Dewar flasks from the traps.

Calculations—

$$\frac{P - P_1 \times 6459 \times 10^{-6} \times 100}{W} - A = \text{percentage of carbon in sample}$$

where  $P$  = pressure in millimeters of CO evolved from sample,

$l$  = volume in millimeters in which gas was measured,

$P_1$  = pressure in millimeters of CO evolved from blank,

$W$  = weight of sample in grams, and

$A$  = percentage of carbon present in 0.5 g flux.

NOTE—Some samples do not require flux, hence no correction is made.

The factor above is calculated for 25°C. If the gas pressure is measured at some other temperature, apply a suitable  $P$  correction.

### DETERMINATION OF CARBON IN METALS BY CONDUCTOMETRIC ANALYSIS

**Principle of the Method**—The principle of this method is based on the combustion of the sample in oxygen during which the carbon in the sample is converted to carbon dioxide. The carbon dioxide is absorbed in a dilute solution of barium hydroxide where the change in conductivity is used as a measure of the carbon content. The method is calibrated by burning A.S. steels of known carbon content or other primary standard such as potassium acid phthalate.

This method has found wide application because of the speed and sensitivity of the analysis. The analysis time is 5 to 8 min. The method is recommended for measuring up to 0.035% carbon based on a 1 g sample, and several times that amount if smaller samples are used. Through special modifications the method may be applied to measuring a few micrograms of carbon.

**Apparatus and Reagents**—Figure 36-40 shows a schematic diagram of an apparatus that is commercially available (manufactured by Laboratory Equipment Co., St. Joseph, Michigan).

**Purification of the Oxygen**—Oxygen is admitted to the apparatus by means of a diaphragm 2-stage regulator valve, through a purifying train consisting of copper oxide at 300°C,  $A$ , magnesium perchlorate, and Ascarite in trap  $B$ , sulfuric acid, magnesium perchlorate, and Ascarite, followed by a flow meter,  $E$ . A pressure gauge,  $C$ , is inserted, as well as an oxygen reservoir,  $D$ .

**Furnace Assembly.**—The furnace consists of a quartz or Vycor tube within which a ceramic crucible is supported on a ceramic pedestal. The pedestal is supported from the furnace base, which can be lowered by simply rotating the weight, *G*, until the handle is released. The seal of the metal base to the quartz tube is made with a rubber "O" ring.

**Conductometric Analyzer.**—This analyzer consists of a sensitive Wheatstone bridge having 2 conductivity dip cells, 1 as a reference cell,  $Q_1$ , and the other a measuring cell,  $Q_2$ . Both cells dip into a dilute barium hydroxide solution, and are balanced in the bridge circuit. The oxygen containing the carbon dioxide bubbles through a mercury trap, *K*, and a diffusion frit, *L*, and into the barium hydroxide contained in the measuring cell. The resistance required to rebalance the bridge is used as a measure of the carbon dioxide absorbed. Since the conductivity of a solution changes with temperature, the cells and analyzer are water jacketed with thermostatic control at a temperature above ambient (40°C.).

**Preparation of the Barium Hydroxide Solution.**—The barium hydroxide solution is prepared as follows: (1) pass nitrogen gas for 45 min. through 17 l. of distilled water, contained in an 18-l. flask. For best results, use distilled water that has

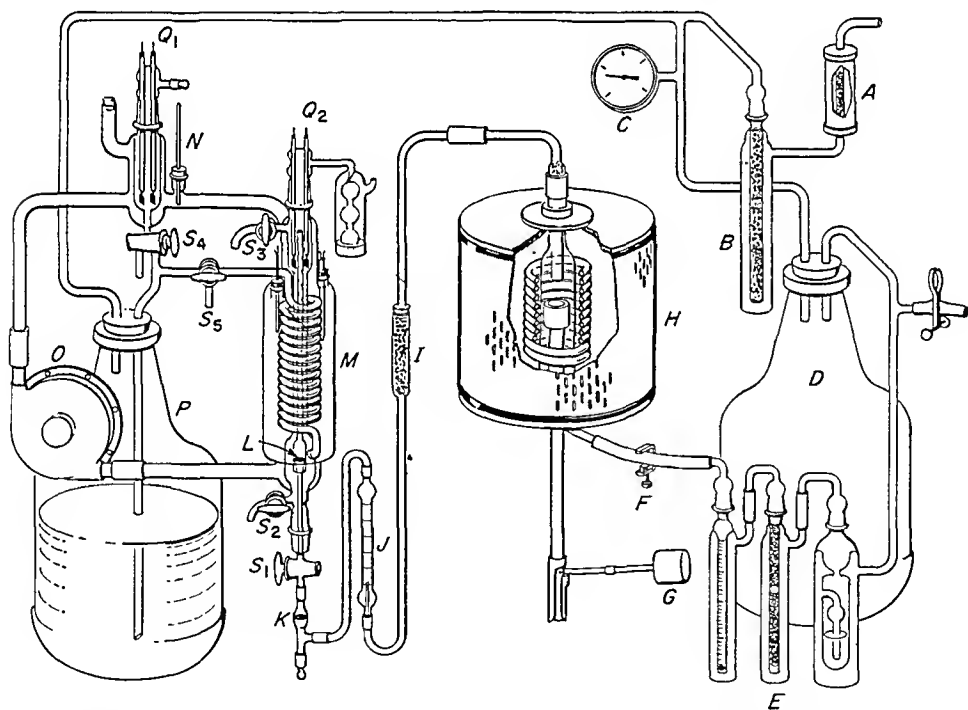


FIG. 36-10. Carbon Apparatus: *A*, Copper Oxide 325°C.; *B*, Magnesium Perchlorate; *C*, Pressure Gauge; *D*, Carboy, Oxygen Reservoir; *E*, Purification Train, Sulfuric Acid, Magnesium Perchlorate, Ascarite, and Flow Meter; *F*, Pinch Clamp; *G*, Weight, Compression of "O" Ring; *H*, Combustion Furnace, Induction Heater, Ceramic Crucible Supported on a Ceramic Pedestal; *I*, Sulfur Trap, Manganese Dioxide; *J*, Flow Meter; *K*, Diffusion Frit with Mercury Trap; *L*, Diffusion Frit; *M*, Tempering Coil for Barium Hydroxide, Water-Jacketed and Thermoregulated; *N*, Thermometer; *O*, Water Pump; *P*, Barium Hydroxide Solution;  $Q_1$ , Conductivity Cell, Reference;  $Q_2$ , Conductivity Cell, Measuring;  $S_1$ ,  $S_2$ ,  $S_3$ , 2-Way Stopcocks;  $S_4$ ,  $S_5$ , 3-Way Stopcocks.

been passed through a cation and anion exchange resin (Amberlite MB1 or equivalent may be obtained from Fisher Scientific Co) (2) boil about 1 l of distilled water for a few minutes to render it free from carbon dioxide. Add 15 g of barium hydroxide to a portion of the water and vacuum filter through a fine glass frit containing some paper pulp. Add this solution to the 17 l of water (3) adjust the volume to 18 l stopper shake and allow to settle for about 1 week before using.

**NOTE**—When small amounts of carbon are being determined the barium hydroxide solution may be diluted to 5 g per 18 l.

**Procedure**—The procedure is as follows (1) turn on the induction heater and the conductometric analyzer and allow sufficient time for the water bath to reach a constant temperature of 40 C (2) close all stopcocks and pinch clamps. Add dilute sodium hydroxide solution to exhaust trap at top of M adjust the oxygen with the regulator to a pressure of 2 to 3 psi (3) open  $S_2$  to permit barium hydroxide to fill the glass tempering coil and the measuring cell Q. Close S and  $S_1$  and open  $S_3$  to drain the barium hydroxide down to constant volume. Close S. Open  $S_1$  partly to adjust oxygen flow. Open  $S_2$  to drain (4) open  $S_4$  to reference cell  $Q_1$  and fill to slightly below the water bath level. Initially both the measuring and reference cells should be flushed out several times. Leave the cell full (5) close pinch clamp F lower furnace base and place crucible with sample weighed to the nearest milligram on the pedestal. Close the furnace open the pinch clamp and then open  $S_1$  slowly until the oxygen flow indicated by the flow meter J reads about 500 ml per min (6) fill the measuring cell with barium hydroxide and adjust the volume as described in step (3). Adjust oxygen flow and flush for about 4 min (7) balance the measuring and standard cell on the Wheatstone bridge as indicated by the coincidence of the lines on the oscilloscope (8) turn on the induction furnace timer so that the sample is fired for 3 min and followed by a 4 min flush. Rebalance the bridge with the decade resistor and record the resistance value (9) open  $S_2$  to drain close F lower furnace base remove crucible and burned sample.

**Standardization**—A graph is established by burning several standard samples of known carbon content and recording the resistance change of the barium hydroxide solution for each. These resistance changes are plotted against the carbon percentages on coordinate paper and should provide nearly a straight line over the range of 0 to 0.30% carbon. For example standards containing 0.10% and 0.30% carbon a 0.105 and 1.0 g sample is used. One scoop of granulated tin (less than 2 g) is used with each combustion of the standard and the sample.

Burn at least 2 different NBS samples weighed to the nearest milligram covering the range of the unknowns and plot the resistance change against the carbon content.

Some metals and alloys require an accelerator in order to effect a complete combustion. In this case the same amount of iron accelerator and tin is burned with the standards as with the unknowns (accelerator has a low uniform carbon content and is available from Laboratory Equipment Co St Joseph Michigan). All corrections are built into the standard curve to eliminate the correction for the carbon content of the accelerator. In general the amount of accelerator used is about 0.5 g.

A new graph is plotted daily.

An alternative method for standardization is the use of potassium acid phthalate

Since the NBS steel standards have an appreciable variation in carbon content within a specified sample, and are relatively high in carbon content, this procedure makes it possible to set up a more accurate standard curve. This is especially helpful in the low carbon levels. By making a standard solution of potassium acid phthalate and dispensing measured amounts into tin cups (available from Laboratory Equipment Co.) by means of a micro syringe, it is possible to prepare about 100 standards in 30 min.

<i>Potassium Acid Phthalate</i>	<i>Volume</i>	<i>= Carbon</i>
<i>Milligrams per 250 cc.</i>	<i>Cubic Centimeters</i>	<i>γ</i>
26.6	0.2	10
53.1	0.2	20
79.7	0.2	30
106.2	0.2	40
132.8	0.2	50

Tin capsules are placed in holes of an aluminum drying block, filled with 0.2 cc. of solution of different concentrations by means of a micro syringe (0.25 cc. volume, Scientific Glass Company, or equivalent), and slowly evaporated to dryness in an oven at 100°C. or less. After the solution has been evaporated, the capsules are flattened with a spatula and rolled up tight into a compact form. In this way, standards can be prepared rapidly and stored for future use. It is always necessary to burn an accelerator with this standard in order to provide a sufficient mass of sample to effect adequate coupling to the induction heater. When such low carbon standards are run, the barium hydroxide solution is used more dilute (5 to 7.5 g. per 18 l.).

**Preparation of the Sample.**—The sample should be used in the form of millings, drillings, or nibbled chips. All samples should be dust-free and degreased in a suitable solvent before analyzing.

## Chapter 37

# PAINT, VARNISH, AND LACQUER

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**Introduction** The term paint sometimes is used in a general way to describe all the surface coatings manufactured by the paint industry. However the term usually is used in a more specific way to designate a highly pigmented coating. In the broadest sense a paint may be defined as a mixture of pigment, binder, thinner, and additives which when spread in a thin film forms a solid adherent surface coating. The pigment gives the paint color and hiding power; the binder acts as a film former which holds the pigment on the painted surface; the thinner brings the pigment-binder mixture to a suitable consistency for application; and the additives impart special properties such as rapid drying. The binder plus the thinner is called the vehicle because together these two components carry the pigment to a surface. The pigment plus the binder (and some additives) make up the nonvolatile matter which becomes the dried paint film.

Based upon the nature of the binder and the amount of pigment in a formulation, surface coatings are commonly classified as paint, varnish, or lacquer. A paint and a varnish both contain binders which form films primarily by oxidation and/or polymerization. A lacquer contains a binder which becomes a film primarily by evaporation of the thinner. A varnish differs from paint in that the varnish is not pigmented; a varnish may be used as a paint vehicle. A lacquer may or may not be pigmented. Even when pigmented, the pigment content of a lacquer is usually much lower than that of a paint. Coatings are also classified according to the type of thinner used in the formulation. Coatings in which organic solvents are the thinner are called solvent type coatings; those in which water is used are known as water type or water-based coatings. The conventional paints, varnishes, and lacquers are examples of solvent coatings. The most important example of the water-based coatings is the latex paint. The definitions of these and other

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terms relating to paint, varnish, and lacquer may be found in A.S.T.M. Designation D16-57.<sup>1</sup>

The number and complexity of the raw materials available to the formulator of surface coatings have increased markedly since the publication of the Fifth Edition of this book in 1939. Almost all the binders and many of the pigments now in commercial use were not considered commercially important enough to be included in the Fifth Edition. Instead of a drying oil and/or a natural resin binder and an inorganic pigment, a modern coating is likely to contain synthetic resins and plasticizers and may contain organic pigments. The synthetic resins found in today's coatings include alkyds, aminos, acrylics, cellulose, epoxies, phenolics, polyesters, silicones, vinyls, and rubber-type resins. In addition many very high molecular weight polymers and copolymers, such as styrene-butadiene and poly(vinyl acetate), are used as the binders in latex paints. Considerable changes in the pigments, thinners, and additives have also taken place. Because of this ever-increasing array of raw materials used in virtually thousands of different combinations, no complete scheme for the analysis of all surface coatings can be given. However, a general analytical approach which will enable one to identify the type of coating with a fair degree of certainty can be presented. Since this chapter is intended to help the non-paint chemist in the identification of the contents of a can labeled "paint," "varnish," or "lacquer," raw material quality control tests are not included.

Strictly speaking, a coating can be considered identified only when each raw material used in the manufacture of the coating has been identified and the relative amounts of each are known. Fortunately, in practice it is rarely necessary to determine the additives present. When the nature and amounts of the pigment, binder, and thinner are known, the coating usually is considered identified. In order to identify and/or determine these three main components, they must be separated from each other. In general, the pigment is first separated from the vehicle, and then the binder is obtained as the nonvolatile portion of the vehicle. The thinner usually is recovered directly from the paint. For analytical purposes it is most convenient to consider all coatings as consisting of a pigment and a vehicle and to present methods for the identification and analysis of the pigment and vehicle portions. In this way unpigmented coatings, such as varnishes and other clear coatings, can be treated as vehicles in the general outline given in this chapter.

## PRELIMINARY INSPECTION OF THE SAMPLE

A great deal of information about a paint product can be obtained simply by reading the label on the can. The label usually will give the name of the manufacturer, the intended use of the product, and some idea of the composition of the paint. If the product is a trade sales item (a product sold at retail directly to the consuming public), very likely a statement of composition will be given on the label. The label analysis generally shows the percentages of pigment and vehicle present and something about the composition of the pigment and vehicle. Some label analyses are sufficiently detailed, for example, to show that the vehicle in the paint is a linseed-soya alkyd resin. This information is very useful in deciding

<sup>1</sup> American Society for Testing and Materials, Philadelphia, Pa., A.S.T.M. Standards on Paint, Varnish, Lacquer and Related Products, 1961.

such questions as what extraction solvent should be used for separating the pigment and vehicle and what methods should be used to analyze the vehicle. Accordingly the label information should be noted as the first step of the analysis. Of course for a sample which does not have a label analysis as much information concerning its history, use, performance, and cost should be obtained elsewhere, if possible.

Before the analysis is started the odor, color and condition of the paint sample should be noted. From the odor one can tell if the coating is a solvent type or a water type coating. For pigmented coatings the color will suggest which pigments are present as discussed in the Section 'Identification and Analysis of Pigments'. The homogeneity of the sample should be checked before a portion is removed for analysis. If the pigment has settled the paint should be thoroughly mixed if skins are present, they should be removed. When possible it is best to retain a portion of the sample for future tests by immediately transferring just the right amount of sample to completely fill a container which should be tightly closed for storage.

## TESTS ON THE TOTAL COATING

### GENERAL

The nonvolatile matter in a pigmented or unpigmented coating is very important in determining the properties and cost of the coating and must be determined as part of every analysis. It is standard practice to obtain the percentage of non volatile matter (abbreviated % NVM) by heating a small sample of the coating in either a convection or vacuum oven and noting the loss in weight. The procedure making use of the vacuum oven is preferred because oxidation of the binder present is less likely. Other properties of the formulation, such as the weight per gallon, the water content, and the flash point, may also be required. These tests are made on the total formulation before any separations are made. The methods given below are based on Federal Test Method Standard 141<sup>2</sup>.

### NONVOLATILE AND VOLATILE CONTENTS

**Procedure**—Place a portion of the thoroughly mixed sample in a stoppered flask or weighing bottle (NOTE 1).

Weigh the sample and container to the nearest milligram. Transfer from 25 to 35 g of pigmented paste or paint or 0.5 to 1.0 g of clear liquid (NOTE 2) to a weighed, flat bottom dish about 8 cm in diameter (NOTE 3) and weigh the container and sample again, and by difference calculate the weight of sample transferred to the dish.

Heat the dish and contents at  $105^{\circ} \pm 2^{\circ}\text{C}$  in a well ventilated, convection type oven for 3 hours or in a vacuum oven under a continuous vacuum of  $29 \pm 0.5$  inches of mercury for 2 hours.

Cool the dish and contents in a desiccator and weigh.

From the weight of residue in the dish and the weight of sample taken, calculate the percentage of nonvolatile or volatile matter as required.

**NOTE 1**—An eyedropper fitted into a cork which in turn fits into a 50 ml Erlenmeyer flask is a convenient way to handle the sample for weighing. A Lunge pipet or syringe is also convenient.

<sup>2</sup> Federal Test Method Standard No. 141 (formerly Fed. Spec. T T P 141b) Paint, Varnish, Lacquer, and Related Materials, Methods of Inspection Sampling and Testing. General Services Administration, Business Service Center, Washington 25 D. C. 1958.

condenser jacket not less than 400 millimeters ( $15\frac{3}{4}$  inches) in length with an inner tube 90 to 127 millimeters ( $\frac{3}{8}$  to  $\frac{1}{2}$  inch) in outside diameter. The end of the condenser to be inserted in the trap shall be ground off at an angle of  $30^\circ \pm 5^\circ$  from the vertical axis of the condenser.

The trap shall be made of well annealed glass constructed in accordance with Fig. 37 I and shall be graduated as shown from 0 to 10 ml in 0.1 ml divisions. The error of any indicated capacity shall be not greater than 0.05 ml. The outside diameters should be preferably 2.5 to 3.5 millimeters ( $\frac{3}{8}$  to  $\frac{1}{4}$  inch) greater than the inside diameters specified.

**Reagent**—The solvent used when testing paint products shall be A.C.S. reagent grade toluene.

**Sample**—The sample shall be thoroughly representative of the material to be tested and the portion of the sample used for the test shall be thoroughly representative of the sample itself. Deviation from this requirement shall not be permitted.

When the sample to be tested contains less than 10% of water, exactly 100 g of the material to be tested shall be placed into the flask and thoroughly mixed with 75 ml of toluene by swirling, proper care being taken to avoid any loss of material.

When the sample contains more than 10% water (by weight), the amount of material used shall be decreased to that which will yield somewhat less than 10 ml of water. (NOTE)

**Procedure**—The connections between the flask, trap, and condenser shall be made by means of tight fitting corks as shown in Fig. 37 I, or standard taper glass ware may be used throughout. The end of the condenser inserted in the trap shall be adjusted to that position which will allow the end to be submerged to a depth of not more than 1 millimeter below the surface of the liquid in the trap after distillation conditions have been established. A drying tube of the calcium chloride type shall be inserted in the top of the condenser tube to prevent condensation of atmospheric moisture in the condenser tube. Heat shall then be applied and so regulated that the condensed distillate falls from the end of the condenser at the rate of from 2 to 5 drops per second.

The distillation shall be continued at the specified rate until no water is visible on any part of the apparatus except at the bottom of the trap. This operation usually requires less than 1 hour. A persistent ring of condensed water in the condenser tube shall be removed by increasing the rate of distillation for a few minutes. The number of ml of condensed water measured by the trap at room temperature multiplied by 100 and divided by the weight of the sample is the percentage of water (by weight) in the material.

**NOTE**—In special cases where the water content exceeds 10% and it is not desirable to reduce the size of the sample to that which will yield somewhat less than 10 ml of water, a distilling tube receiver graduated from 0 to 25 ml may be used. This tube shall be graduated from 0 to 2 ml in 0.1 ml and from 2 to 25 ml in 0.2 ml.

## FLASH POINT

The flash point of a material is the temperature at which it can be ignited by a small flame. There are two standard methods by which the flash point of a paint can be determined: the open cup method and the closed cup method. The open cup method is used chiefly to determine whether the paint must be classified as

"inflammable," and therefore, required to have a "Red Label" for interstate shipping. Complete directions for determining the flash point by means of the Tag Open Cup apparatus can be found in A.S.T.M. Method D1310-59T. A procedure for the open cup method is given in the chapter on Petroleum and Petroleum Products in this volume.

The closed cup method is most frequently specified in governmental and industrial specifications as a measure of the flammability hazards of a coating material. The flash point of a coating material by the closed cup method is commonly determined by either one of two methods. One method is by the use of the Pensky-Martens Closed Cup Tester. The details of this method are given in A.S.T.M. Method D93-61 and in Federal Test Method Standard 141, Method 4293. This method is intended for determining the flash point of pigmented coating materials that require stirring to obtain uniform distribution of heat. The other closed cup method, described in A.S.T.M. Method D56-61 and in Federal Test Method Standard 141 Method 4291, is by means of the Tag Closed Tester. This method can be used for all mobile liquids, such as varnishes and thinners, which flash below 79°C. (175°F.). The Tag Closed Tester can likewise generally be used to determine the flash point of pigmented materials which do not have an unusually high viscosity. Detailed procedures for both closed cup methods are given in the chapter on Petroleum and Petroleum Products in this volume.

## SEPARATION OF PIGMENT, BINDER, AND THINNER OF SOLVENT TYPE COATINGS

### GENERAL

The most fundamental process in the analysis of a pigmented coating is the separation of pigment and vehicle. Depending upon whether the coating is a solvent type or water type, different treatment is required to resolve the pigment and vehicle. For solvent paints the standard methods involve diluting the paint with a solvent mixture in which the vehicle is soluble and in which the pigment is insoluble. After dilution the paint is centrifuged to remove the pigment. The pigment content is determined by drying and weighing the separated pigment.

It should be pointed out that complete separation of pigment and vehicle is seldom achieved. Usually a small amount of vehicle is left with the pigment portion through adsorption of the vehicle on pigment particles. On the other hand, some pigment particles stay with the vehicle in the form of a colloidal dispersion. The separated pigments and vehicles also may be different from the original pigment and vehicle used in the manufacture of the paint because of chemical reactions of the components. For example, in paints containing zinc oxide, some zinc may be found in the vehicle portion due to reaction of the basic zinc oxide with an acidic binder.

### ISOLATION AND DETERMINATION OF PIGMENT

*Extraction Mixture.*—The solvent mixture used for the extraction of the vehicle from the pigment depends upon the particular pigments and vehicle in the coating. The extraction solvents recommended for certain groups of pigments in various vehicles as given in Federal Test Method Standard 141, Method 4021 are listed below (also see NOTE 2, p. 1623):

*Pigment Groups*

- |   |  |
|---|--|
| <b>I</b> Whites, all<br>Ultramarine blue<br>Yellow ochre<br>Yellow iron oxide<br>Chrome yellow and orange<br>Molybdate orange<br>Metallic brown<br>Umbers and siennas<br>Mineral red iron oxide<br>Bright red<br>Indian red<br>Venetian red<br>Chromium oxide green<br>Carbon black | <b>II</b> Lampblack<br>Carbon black<br>Toluidine<br><br><b>III</b> Chrome green<br>Iron blue |
|---|--|

*Extraction Solvents*

- |  |   |
|--|---|
| <b>A</b> 10 vols ethyl ether<br>6 vols benzene<br>4 vols methanol<br>1 vol acetone<br><br><b>B</b> 3 vols toluene<br>4 vols absolute ethanol<br>3 vols acetone | <b>C</b> 1 vol toluene<br>1 vol acetone<br><br><b>D</b> 1 vol ethyl ether<br>3 vols petroleum ether |
|--|---|

*Selection of Extraction Solvents*

COATING OR VEHICLE	PIGMENT GROUP	EXTRACTION SOLVENT
1 Paint Enamel Lacquer Paste Color-in-Oil	I	Mixture <i>d</i>
2 Linseed Oil Vehicles	I II III	Petroleum ether when mixture <i>d</i> is not satisfactory Petroleum ether Mineral spirits followed by hot absolute alcohol (See NOTE, p 1623)
3 Varnish and Resin Vehicles	III	Mixture <i>B</i>
4 Cellulosic lacquers and vinyl paints	I and II (except for toluidine)	Extraction mixture <i>C</i> May be necessary to modify with other appropriate solvents if separation is unsatisfactory
5 Toluidine Enamels	II	Mixture <i>D</i> In some cases the ratio of ethyl ether may have to be increased

**NOTE.**—Group III pigments may be separated from linseed oil vehicles in the following way: Place 10 to 15 g. of sample in a weighed four-ounce screw cap bottle. Add 5 ml. of mineral spirits, replace cap, and shake thoroughly. Remove cap, add 45 ml. of hot absolute ethanol, and mix thoroughly by stirring with a glass rod. Keep the bottle and contents in a hot water bath while stirring. Remove the stirring rod and wash any adhering pigment back into the bottle with hot alcohol. Centrifuge while hot for about 2 minutes. Pour off the clear solvent and oil layer and rinse the bottle with hot alcohol without disturbing the pigment cake. Repeat the extraction three times. Dry the bottle and contents as below and calculate the pigment content.

**Procedure.**—Weigh about 15 g. of sample (to nearest 0.1 g.) into a four-ounce bottle with a screw cap (NOTE 1). Add 50 to 60 ml. of the extraction mixture indicated above. Screw cap onto bottle and shake until thoroughly mixed. Place the bottle in a centrifuge and counterbalance the container of the opposite arm with another sample or with a bottle containing water. Centrifuge until well settled. Decant the clear supernatant liquid and add about 50 ml. of extraction mixture. Shake vigorously to redisperse the pigment. Centrifuge as before. Repeat once more. (A final wash with ethyl ether hastens the drying process.) Save all the decanted liquid portions if the binder is to be recovered from the extraction liquid.

Initially dry the pigment by passing a gentle current of air into the bottle. Replace the cover and shake the bottle to break up the pigment. Remove the cover and place in an oven at  $105^{\circ} \pm 2^{\circ}\text{C.}$  for 2 hrs.

Cool, weigh, and calculate the percentage of pigment.

When a pigment analysis is required, transfer all of the pigment to a mortar. Grind with the pestle, stopping occasionally to scrape the sides of the mortar with a spatula to thoroughly mix the pigment since stratification of the pigment may occur during centrifugation. Pass the powder through a No. 80 sieve to remove any "skins" and save the pigment in the four-ounce screw cap bottle.

**NOTE.**—1. The authors have found that four-ounce screw cap bottles about 11 cm. in height and 4.5 cm. in diameter to be more convenient than centrifuge tubes. If such bottles are unavailable, the sample may be placed in a centrifuge tube and mixed with a glass stirring rod where the above procedure calls for shaking. Crown No. 9-456 bottles from Crown Glass Corporation have been found to be satisfactory. An International Centrifuge, size 1, type C, also has been found to be satisfactory.

2. Suggestions for other pigment-vehicle combinations may be found in reference 3.

### ISOLATION OF VEHICLE (SUPERCENTRIFUGE)

**General.**—This procedure is satisfactory for most materials except black and certain other organic pigments.

**Procedure.**—About 75 ml. of a well-mixed paint are placed in the bowl of a laboratory supercentrifuge. If the viscosity is too high, reduce with suitable solvent to the consistency of an ordinary enamel. Record weight of solvent added to the weight of total paint in this case.

The material is then revolved at approximately 40,000 r.p.m. for a period of 30 min. or until clear. The isolated vehicle is then removed and placed in a well-stoppered bottle. Every precaution should be taken to prevent evaporation of solvent from the vehicle. The isolated vehicle is held and used for other tests.

### ISOLATION OF THINNER (VOLATILE MATTER)

**General.**—Two procedures for the isolation of the volatile matter in a coating are regarded as standard; one involves ordinary distillation and the other steam distillation. Steam distillation is the more generally applicable of the two because

all times. Vacuum distillation may be used and is preferred, particularly where nonvolatile ingredients having low decomposition temperatures are involved.

Thoroughly mix and examine the distillate for the properties required of the volatile matter in the coating material.

### ISOLATION AND DETERMINATION OF THE BINDER (NONVOLATILE VEHICLE) CONTENT

**General.**—The binder may be obtained by evaporation of the volatile material from the isolated vehicle or from the decanted liquid portions remaining after the isolation of the pigment. When the binder (nonvolatile vehicle) is to be recovered for identification purposes, both methods are equally satisfactory. When a quantitative analysis of the binder is to be made, it is convenient to make the analysis via the isolated vehicle as obtained in the section "Isolation of Vehicle (Supercentrifuge)," above.

**Procedure by Ordinary Centrifuge.**—Proceed as in section on Isolation and Determination of Pigment (page 1621) and retain all of the decanted liquid.

Combine the liquid portions and evaporate on a steam bath until all volatile matter has been removed. The remaining nonvolatile portion is the binder.

**Procedure by Supercentrifuge.**—Isolate the vehicle by the supercentrifuge method.

Determine the nonvolatile matter in the isolated vehicle as given in the sections on Nonvolatile and Volatile Contents (page 1618) or Nonvolatile Content (page 1642). See the section on Nonvolatile and Volatile Contents for a discussion of the factors involved in obtaining an accurate nonvolatile content determination.

The nonvolatile portion of the vehicle is reported as the per cent nonvolatile, usually abbreviated as %NVV. The nonvolatile vehicle is the binder.

### CALCULATION OF BINDER OR PIGMENT CONTENTS

**General.**—The percentage of nonvolatile matter in the total paint (NVM), the percentage of binder in the vehicle (NVV), and the percentage of binder in the total paint are related through the equation given below. When any two of the three quantities are known, the third may be calculated.

Let:  $A = \%NVM$  = nonvolatile matter in total paint

$B = \%NVV$  = nonvolatile vehicle or binder content of vehicle

$C = \%$  of binder (or vehicle solids) in total paint.

Then:

$$\frac{100 - B}{B} = \frac{100 - A}{C}$$

**Binder (or Vehicle Solids) Content of Total Paint.**—

$$C = B \frac{(100 - A)}{(100 - B)}$$

**Pigment Content.**—

$$\% \text{ Pigment in Total Paint} = \%NVM - C, \text{ or}$$

$$\% \text{ Pigment in Total Paint} = \frac{(A - B)100}{100 - B}$$

## ISOLATION AND DETERMINATION OF BINDER

The binder (plus additives) may be obtained as the nonvolatile portion of the vehicle separated above. See Sections on pages 1618, and 1642.

## DETERMINATION OF THE WATER CONTENT

The water in a latex or emulsion paint may be determined as described on page 1619.

## IDENTIFICATION OF THE BINDER

## GENERAL

As the film-forming part of a surface coating, the binder imparts many of the special properties of a particular formulation. For this reason, the identification of the binder is usually the most important step in the analysis of a coating. As indicated earlier, the binder may contain drying oils, natural or synthetic resins, high-molecular weight polymers, and plasticizers. Synthetic resins are actually polymers, and whether a binder is called a resin or a polymer is dictated by common usage. Virtually all of the polymers found in commercial plastics and in rubber products have been used as binders in modern coatings. Accordingly, the information given in the chapters on the analysis of plastics and rubber in this volume may aid in the identification of a particular binder. The present chapter is confined to the presentation of methods for those materials most likely to be found in the binder portion of finished paint, varnish, and lacquer products.

It must be emphasized that the binders of lacquer formulations almost always contain monomers in addition to the polymeric film-former. The monomers are called plasticizers and are added to improve the flexibility of the lacquer film. (Other low-molecular weight materials, such as drying oils and resins, also may be present in a product labeled a "lacquer" and may act as plasticizers in addition to performing other functions. For the purposes of this discussion, monomers, oils, and resins are all included in the term "plasticizer.") In order to fully identify a lacquer binder, both the polymer and plasticizer portions present must be identified. Identification of the types of polymer and plasticizer present sometimes may be made by tests applied to the total binder, but usually it is necessary to separate the two before each can be fully characterized. Methods for their separation depend upon the particular polymers and plasticizers present. Consequently, the total binder should be tested first by the methods given for the polymers below in order to obtain some idea of which polymer is present. Then, the polymer-plasticizer separation may be made by the procedure given under the heading of the polymer in the section on Analysis of the Vehicle, p. 1641.

The most common lacquer polymers include cellulose nitrate, cellulose acetate, cellulose acetate-butyrate, ethyl cellulose, poly(vinyl chloride), poly(vinyl chloride-acetate), and poly(methyl methacrylate). The common plasticizers are phthalate esters, aryl phosphates, and low molecular weight alkyds. In contrast with the lacquers, the binders of paints and varnishes usually do not contain plasticizers; instead they almost always contain oils which are self-plasticizers. Common paint and varnish binders include oil-modified alkyds, drying oils, drying oils modified with rosin derivatives or phenolic resins, oil modified alkyds blended with melamine and/or urea resins, styrenated alkyds, and epoxides. The binders of latex



TABLE 37-1. IDENTIFICATION SCHEME FOR POLYMERS, RESINS, AND OILS BASED ON INFRARED ABSORPTION BANDS

<i>Part I—Ester Types (Carbonyl Band at 5.8 Microns)</i>		
Carbonyl Band at 5.8 Microns	6.3, 6.7 Present (Aromatic)	6.5, 8.2 7.7, 8.1, 13.8 7.8, 8.9, 9.3, 13.5, 14.2 7.9, ~9.0, 11.5, 13.8 8.1, 8.5, 12.1 12.3, 12.8, 14.3 13.2—13.4, 14.3 Polyurethanes Isophthalate Alkyds and Polyesters Phthalate Alkyds and Polyesters Terephthalate Alkyds and Polyesters Bisphenol Epoxy Esters Vinyl Toluene Esters Styrenated Esters
	6.3, 6.7 Absent (Aliphatic)	6.85, 8.1 ( <i>w</i> ), 8.6 7.0, 7.26, 8.1 7.0, 14.5 ( <i>b</i> ) 8.1, 8.55, 12.2 9.0—9.5 ( <i>b</i> ) 9—10 ( <i>s</i> ), 7.9, 8.05 9—10 ( <i>s</i> ), 8.0 ( <i>b</i> ) Oils Poly(vinyl acetate) Poly(vinyl chloride-acetate) and Poly(vinylidene chloride-acetate) Rosin Esters Cellulose Esters Polymethacrylates Polyacrylates
<i>Part II—Non-Ester Types (No Carbonyl Band at 5.8 Microns)</i>		
No Band at 5.8 Microns	6.3, 6.7 Present (Aromatic)	3.0, 8.2, 11—15 7.0, 9—10 ( <i>s</i> ) 8.1, 8.5, 12.1 12.3, 12.8, 14.3 13.2, 14.3 Phenolics Phenyl Siloxane Bisphenol Epoxides Poly(vinyl toluene) Polystyrene
	6.3, 6.7 Absent (Aliphatic)	3.0, 9.0—9.6 4.4 6.1, 6.5 6.1, 7.9, 12.0 6.5, 12.1 6.5, 12.3 7.0, 7.4, 9.5 ( <i>b</i> ) 7.0, 7.5, 14.5 ( <i>b</i> ) 7.9, 9—10 ( <i>s</i> ) 9.0 Poly(vinyl alcohol) Polyacrylonitrile Urea-formaldehyde and Polyamides Cellulose Nitrate Benzoguanamine-formaldehyde Melamine-formaldehyde Poly(vinylidene chloride) Poly(vinyl chloride) Methyl Siloxane Polyvinyl Ethers and Acetals, Cellulose Ethers

KEY: (*w*), weak; (*s*), strong; (*b*), broad.

and consequently, the unknown is placed in Part I of the table. Next, it is necessary to note if bands at about 6.3 and 6.7 microns are present. These bands also are present in Fig. 37-2, and consequently, the unknown has been narrowed down to something given in the upper half of Part I. At this point the unknown has been identified as an aromatic ester. For more detailed identification, the strong bands from 6.5 microns and higher become important. The strongest band in this region is at 7.8 or 7.9; next strong band is at 8.8 or 8.9; next at about 9.3; next at about 13.4; and next at about 14.3. Comparison of these numbers with those given in Table 37-1 shows that the unknown is probably a phthalate alkyd (or polyester) or a styrenated ester. Table 37-2 lists a phthalate alkyd as spectrum number 1 and a styrenated phthalate alkyd as spectrum number 2. Comparison of the spectrum of the unknown with the two reference spectra at the end of the chapter shows that the unknown's spectrum matches that of a styrenated phthalate alkyd. This matching of spectra is considered sufficient evidence to establish that the unknown binder is primarily a styrenated phthalate alkyd.

The above example serves to demonstrate both the utility and the limitations of the infrared method. By infrared it was very easy to show that the binder was a phthalate alkyd, and it was equally simple to show that the alkyd was styrenated,

<i>Binder Materials</i>	<i>Spectrum Number</i>
Alkyd Resins	
Linseed Glycerol Phthalate (film)	1
Styrenated Soya Tung Glyceryl Phthalate (film)	2
Vinyl Toluenedated Soya Tung Glycerol Phthalate (film)	3
Alkyd-Melamine Urea Blend (film)	4
Amino Resins	
Melamine Formaldehyde, <i>n</i> -Butylated (film)	5
Urea-Formaldehyde, <i>n</i> -Butylated (film)	6
Benzoguanamine-Formaldehyde (film)	7
Oils	
Linseed Oil, Raw (liquid)	8
Oiticica Oil (liquid)	9
Tung Oil (liquid)	10
Castor Oil, Dehydrated (liquid)	11
Phenolic Modified Linseed Oil Varnish (film)	12
Phenolic Resins	
<p><i>p</i>-tert -Butylphenol-Formaldehyde (1.4 mg in KBr)</p>	13
<p><i>p</i>-Phenylphenol-Formaldehyde (1.2 mg in KBr)</p>	14
Rosin Derivatives	
Glyceryl Ester of Rosin (Ester Gum) (film)	15
Maleic Rosin Ester (film)	16
Zinc Resinate (film)	17
Pentaerythritol Dehydrated Castor Oil Rosin Varnish (film)	18
Epoxides	
Bisphenol Type with Epoxide Equivalent of 200 (1 mg in KBr)	19
Bisphenol Type with Epoxide Equivalent of 500 (1 mg in KBr)	20
Epoxide Ester of Castor Oil (film)	21
Cellulosics	
Cellulose Nitrate (film)	22
Cellulose Nitrate, Phthalate Ester Plasticized (film)	23
Cellulose Acetate (film)	24
Cellulose Acetate-Butyrate (film)	25
Vinyls	
Poly(vinyl chloride) (film)	26
Poly(vinyl chloride), Phthalate Ester Plasticized	27
Poly(vinyl chloride-acetate) (film)	28
Poly(vinyl chloride-acetate-maleate) (1% Maleic Acid) (film)	29
Acrylics	
Poly(methyl methacrylate) (film)	30
Poly(methyl methacrylate), Phthalate Ester Plasticized (film)	31
Poly(methyl methacrylate butyl methacrylate) (film)	32
Plasticizers	
Di(2 ethylhexyl)phthalate (liquid)	33
Butyl Benzyl Phthalate (liquid)	34
Epoxidized Soya Oil (liquid)	35
Tricresyl Phosphate (liquid)	36
Latex Polymers	
Poly(styrene-butadiene) (film on AgCl)	37
Styrene-Acrylonitrile-Acrylate Terpolymer (film on AgCl)	38
Poly(vinyl acetate) (film on AgCl)	39

(Footnote on facing page)

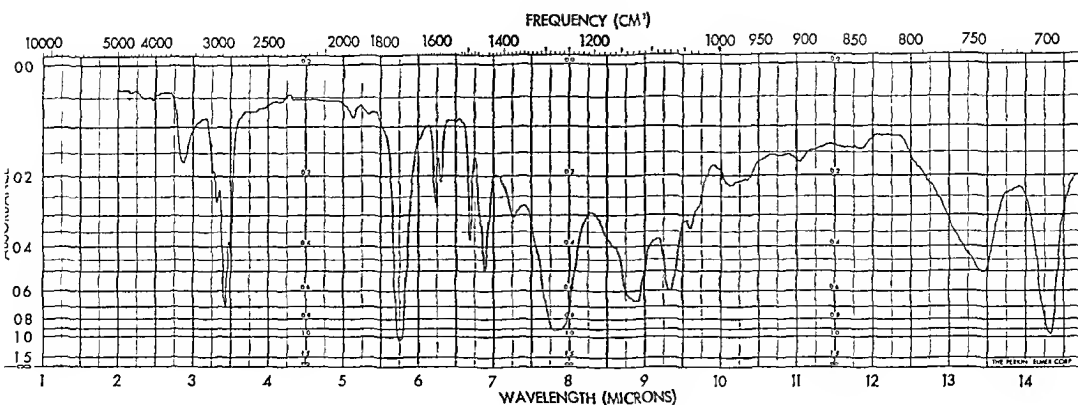


Fig. 37-2. Spectrum of Unknown Binder.

and not, for example, vinyl toluenated. To distinguish between a styrenated and vinyl toluenated alkyl is of practical importance with this type of binder, and it is very difficult to do so by chemical means. Further, the infrared procedure requires less than an hour of operator time. Unfortunately, in the case of alkyds, one limitation is that their infrared spectra reveal almost no information about the fatty acid and polyhydric alcohol part of the alkyd. Once it is known the binder is an alkyd, however, it may be saponified and the constituents can be determined as described in the section on Alkyds of this chapter. A second limitation of the infrared method is a general one and is reflected in the use of the qualifying term "primarily" in the above identification. "Primarily" should be used when only an infrared identification is made because there is always the possibility that a few per cent of another material which is not revealed in the spectrum of the binder may be present.

Several excellent papers on the use of infrared spectroscopy for the identification of polymers and resins have appeared in the literature.<sup>13</sup> Recently, a comprehensive paper on "An Introduction to the Use of Infrared Spectroscopy in the Field of Paints and Coatings" has been prepared by the Technical Committee of the Chicago Society for Paint Technology specifically for the practicing paint analytical chemist.<sup>14</sup> This paper presents the elementary theory of infrared spectrophotometry, techniques for the preparation of samples for infrared analysis, types of apparatus and accessories available, and methods of qualitative and quantitative analysis by infrared. Systematic reviews of the qualitative, quantitative, and research applications of infrared as applied to the paint industry with 263 references are given. Reference spectra of 121 binder materials, 46 pigments, 22 sol-

<sup>13</sup> Weinberger, L. A. and Kagarise, R. E., *Infrared Spectra of Plastics and Resins*, U. S. Dept. of Commerce, O. T. S. Bulletin No. PB111438, 1954; Hausdorff, H., *Analysis of Polymers by Infrared Spectroscopy*, Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy, 1951. (Reprinted by Perkin-Elmer Corp., Norwalk, Conn.).

<sup>14</sup> Brown, W. H., Ansel, R. E., McGinness, J. D., and Lucchesi, C. A., *Offic. Dig. Federation Societies Paint Technology* 33, Part II of March Issue, 1961.

(Footnote to Table 37-2)

\* The state of the sample used to obtain the infrared spectrum is given in parenthesis after the name of the material. The term "film" means the sample was cast from solution as a film on sodium chloride. "Film on AgCl" means the film was cast on silver chloride, and "KBr" means the material was dispersed in a potassium bromide pellet. The exact procedures are given at the end of the chapter in the section on Infrared Spectra.

TABLE 37-3. QUALITATIVE AND SPOT TESTS FOR POLYMERS AND RESINS

<i>Test</i>	<i>Binder Materials Giving Positive Test</i>	<i>Remarks</i>
Nitrogen (Sodium Fusion)	Melamine-Formaldehyde Urea-Formaldehyde Cellulose Nitrate Polyamides Acrylonitrile Polymers Sulphonamides Polyurethanes	Vehicles separated from paints containing Prussian blue or phthalocyanine blue may give positive test due to presence of these pigments.
Halogen (Sodium Fusion and Beilstein Test)	Poly(vinyl chloride) Poly(vinyl chloride-acetate) Poly(vinylidene chloride) Chloroprene Chlorinated Rubber Rubber Hydrochloride	Residues of chlorinated solvents may cause positive test.
Sulfur	Polysulfide Rubber Sulphonamides	See Chapter on Rubber Products
Formaldehyde	Melamine-Formaldehyde Urea-Formaldehyde Phenol-Formaldehyde	Phenolic modified rosin may give negative test.
<i>o</i> -Phthalate (Phenolphthalein)	Phthalate Alkyds Phthalate Polyesters Phthalate Plasticizers	Isophthalic and terephthalic alkyds and polyesters give negative tests. Cellulose nitrate interferes.
<i>o</i> -Phthalate (Quinizarin)	Same as above	Same as above, but cellulose nitrate does not interfere.
Acetate	Poly(vinyl acetate) Poly(vinyl acetate-maleate) Poly(vinyl alcohol) Poly(vinyl acetal) Cellulose Acetate	Poly(vinyl chloride-acetate), Poly(vinyl butyral), Poly(vinyl acetate-propionate), Poly(vinyl acetate-butyrate) may give negative tests.
Cellulosics	Cellulose Cellulose Acetate Cellulose Acetate-Butyrate Methyl Cellulose	Cellulose nitrate does not give positive test
Nitrate	Cellulose Nitrate	Melamine, urea, polyamide, acrylonitrile, acrylate, and vinyl resins give negative tests. Coumarone resins and oxidizing agents interfere.
Epoxide (Foucry)	Bisphenol-Type Epoxy Resins and Varnishes	Epoxidized oils may give negative test. Phenolics and nitrogen resins do not interfere.

TABLE 37-3 (Continued)

<i>Test</i>	<i>Binder Materials Giving Positive Test</i>	<i>Remarks</i>
Epoxide (Swann)	Same as above	Same as above
Phenolic (Gibbs)	Phenol Formaldehyde Phenolic Varnishes Furfural-Phenol Resins	Bisphenol type epoxides and epoxy resin esters, coumarone-indene resins, and some alkyls give positive tests
Phenolic (Swann)	Same as above	Bisphenol type epoxides do not interfere Alkyls give negative tests
Styrene	Polystyrene Styrene-Butadiene Styrenated Alkyls Styrenated Oils	Phenolics and epoxides do not interfere Vinyl toluenated alkyls and oils give positive tests
Urea	Urea-Formaldehyde	Melamine, polyurethane and alkyl resins do not give positive test Some heat reactive phenolics may interfere
Melamine (Swann)	Melamine-Formaldehyde	Urea, polyurethane, and alkyl resins do not interfere
Melamine (Feigl)	Melamine-Formaldehyde	Urea gives negative test but cellulose nitrate gives positive test
Rosin (Liebermann- Storch)	Rosin Rosin Esters Metal Salts of Rosin Maleic Modified Rosin Tall Oil Rosin-Modified Phenolics Rosin-Modified Alkyls	Other natural resins give similar colors and interpretation must be made cautiously Highly polymerized or oxidized oils and coumarone-indene resins may give positive test
Methacrylates	Poly(methyl methacrylate)	Poly(methyl acrylate) and cellulose nitrate give negative tests
Chlorinated Rubber	Chlorinated Rubber, and Substances having terminal $-\text{CH}_2\text{Cl}$ or $-\text{CHCl}_2$ groups	Chloroprene gives negative test Poly(vinyl chloride) gives positive test

NOTE.—Chromotropic acid (1,8-dihydroxynaphthalene-3,6-disulfonic acid) may be replaced with veratrole (1,2-dimethoxybenzene).

**Ortho-Phthalate.**—*Ortho*-phthalate alkyds have been detected by the formation of a white sublimation upon pyrolysis of the resin, by the formation of fluorescein when treated with resorcinol, by the formation of quinizarin when treated with hydroquinone, and by the formation of phenolphthalein when reacted with phenol.<sup>5, 19, 21</sup> The latter method is most reliable, but in the presence of cellulose nitrate the test yields a dark water-soluble material which obscures the phenolphthalein color. Consequently, if it is suspected that cellulose nitrate is present in the sample, phthalate must be detected in some other way. For this reason two procedures are given below. If the dark material appears as a result of the first test (phenolphthalein), then the second test (quinizarin) must be made.

**Phenolphthalein Procedure.**—Add 2 to 3 g. of phenol (NOTE 1) and 5 drops of concentrated sulfuric acid (sp. gr. 1.84) to 1 g. of binder in a test tube. Bring to a gentle boil and keep boiling for 15 sec. Cool, dilute with water, and mix by inverting the tube several times. Wait about 2 min. and add a 10% solution of potassium hydroxide until the mixture is alkaline.

The appearance of the pink color of phenolphthalein as the solution is made alkaline is a positive test for *ortho*-phthalate.

**Quinizarin Procedure.**—Place a drop of vehicle or a piece of binder in a 25 x 150 mm. borosilicate glass test tube and add about 1 g. of hydroquinone and 2 ml. of concentrated sulfuric acid (sp. gr. 1.84). Place the tube and contents in a glycerol bath initially at room temperature (NOTE 2) and heat the bath to 190°C. Remove the test tube, cool, and cautiously add 25 ml. of water. Then add 20 ml. of benzene and shake the mixture.

A yellow color in the benzene layer is a positive test for *ortho*-phthalate. For confirmation, transfer part of the benzene layer to another test tube and shake with dilute aqueous alkali. A violet color results when *ortho*-phthalates are present.

NOTES.—1. It is convenient to melt the phenol first and then add a few milliliters with an eye dropper.

2. Alternatively, the test tube may be fitted with a thermometer and slowly heated to 190°C. over a small Bunsen flame.

**Acetates.**—No method for the detection of acetate binders is regarded as standard. The method given below has been used by the authors.

**Procedure.**—Warm a piece of binder (see NOTE) in about 1 ml. of dilute hydrochloric acid for 10 min., cool, and add a drop of 5% solution of lanthanum nitrate, 1 drop of 0.1 M iodine, and enough concentrated ammonia to make the solution basic. A blue or brown color quickly develops in the binder if acetate is present.

NOTE.—Best results are obtained when the dried binder is pulverized before it is added to the acid.<sup>16</sup>

**Cellulosics.**—There are no tests for cellulosics which are regarded as standard. The method given below<sup>16</sup> has been found to be useful by the authors.

**Procedure.**—Place a piece of the binder and a drop of concentrated phosphoric acid in a micro 15 x 125 mm. test tube fixed in an asbestos board. Cover the mouth of the test tube with a piece of filter paper moistened in aniline acetate solution (10% of aniline in 10% acetic acid) and weigh down with a watch glass. Cautiously heat test tube with a micro flame for 30 to 60 seconds.

<sup>21</sup> Swann, M. H., Anal. Chem. 29, 1352, 1957.

A red fleck appears on the filter paper if cellulose or a cellulose derivative is present. Only a vivid red color should be taken as a positive test. Many binders such as cellulose nitrate, bisphenol epoxides, and polymerized oils give an orange color. This orange color should not be mistaken as a positive test. It is best to run a known (as cellulose acetate) along with the unknown to help in the interpretation of the color.

**Nitrates**—The diphenylamine test for nitrate is the standard method for detecting cellulose nitrate. Tests by the authors on clear blends of cellulose nitrate with acrylics with ureas and with alkyls indicate that as little as 1% cellulose nitrate in these blends can be detected easily with diphenylamine. Strong oxidizing agents such as chromites in a pigmented coating interfere by over oxidizing the reagent and causing the formation of a brown to black color.

**Reagent**—Prepare 85% sulfuric acid by mixing 100 ml of acid (sp gr 1.84) with 30 ml of distilled water. Then add 100 mg of diphenylamine to 100 ml of the 85% acid solution.

**Procedure**—Place a few drops of the reagent on the surface of a dried film (or chips) of the binder in the depression of a white porcelain spot plate.

The immediate appearance of an intense blue color is a positive test for nitrate. The blue color gradually disappears and a blackened spot remains after a few minutes.

**Epoxides**—The ASTM is currently studying three Foucroy tests<sup>2</sup> and a spot test proposed by Swann<sup>3</sup> for their use in detecting bisphenol type epoxides in resin mixtures. The two most promising tests are given below.

**Foucroy Nitric Acid Procedure**—Dissolve 0.1 g of binder in 10 ml of concentrated sulfuric acid by shaking at room temperature. To 1 ml of the sulfuric acid solution add 1 ml of 63% nitric acid (63 ml HNO<sub>3</sub> sp gr 1.42 with 37 ml water) and allow the mixture to stand for 5 min.

Pour the mixture into 100 ml of 5% NaOH (5 g NaOH pellets plus 95 ml water) with stirring. Note the color when the heavier (more viscous) acid solution strikes down into the alkaline solution. A positive result usually follows when a reddish color is produced whereas a negative test results if only a whitish cloud is formed. However the final color of the total solution obtained upon stirring should be the criterion of the test. A positive test is indicated by an orange-red solution (sometimes almost totally red) which forms immediately.

**Swann Spot Test Procedure**—Dissolve about 0.1 g of binder in about 5 ml of concentrated sulfuric acid. If necessary a water bath at 40 to 50°C may be used to effect solution. The sample in sulfuric acid is then diluted with more concentrated sulfuric acid (or a small amount is added dropwise to about 5 ml of acid in a test tube) until the color of the diluted sample approximates that of 0.1 M potassium dichromate solution (see Note).

Dip a glass stirring rod into the acid solution and streak the rod across a piece of filter paper suspended in a horizontal position. If bisphenol type epoxy resins are present a bright purple color develops in less than a minute eventually the color turns blue.

**NOTE**—Dilution to an approximate color makes the test specific for epoxy resins. High concentrations of other binder materials such as fish oil, tung or oiticica oil, cyclopentadiene treated linseed oil, rosin, rosin esters, and some phenolic resins produce pink to red colors which may cause confusion.

<sup>2</sup> Ridd, H. W. and Zonsveld, J. J. *Oil and Colour Chemists Assoc.* 39: 314, 1956.

<sup>3</sup> Swann, M. H. *Offic. Dig. Federation Soc. Paint Technology* 30, 1247, 1958.

**Phenolic Resins.**—Five tests for phenolic resins have been subjected to cooperative study: that of Kappelmeier with 2-nitro-4-aniline, that of Gibbs with 2,6-dibromoquinone-4-chlorimide, that of Moir with *p*-nitroaniline, that of Millon with mercurynitric acid, and that of Swann with nitrous acid. From a comparative study of the first three tests, in which phenol formaldehyde resins, modified phenolic resins, and phenolic varnishes were involved, the Association of Paint Research in the Netherlands concluded that on the whole the Moir Method was "to be preferred but that in many cases the Gibbs method also gave satisfactory results."<sup>24</sup> A current A.S.T.M. study of the Gibbs, Millon, and Swann procedures, involving epoxides as well as phenolics, has already shown that the Gibbs and Millon methods give positive results for bisphenol-type epoxides and epoxy resin esters. Thus far, the Swann method appears to be free of interference from bisphenol-type epoxides.

A method for distinguishing between phenolics and epoxides is particularly valuable because in some cases a small amount of phenolic resin cannot be seen in the infrared spectrum of a resin mixture containing the two resins. For this reason the Swann method as well as the more generally recognized Gibbs method<sup>2,25</sup> is given below.

**Gibbs Procedure.**—Place about 1 milligram of binder in a micro test tube fixed in an asbestos board. Cover the mouth of the test tube with a disk of filter paper which has been bathed in a saturated ether solution of 2,6-dibromoquinone-4-chlorimide and then dried (see NOTE). Heat the bottom of the test tube gently at first and then more strongly until fumes are produced, and make the fumes come into contact with the reagent paper. Several minutes heating are required in most cases. Cool the paper and expose it to ammonia vapor. A blue stain is a positive test for phenol.

**Swann Procedure.**—Place 40 ml. of benzene in a 50-ml. glass-stoppered graduate and add 50 mg. of the binder to be tested. If the binder is insoluble in benzene, dissolve it in 20 ml. of butyl acetate and then add 20 ml. of benzene.

Add 10 ml. of 3.6 *N* sulfuric acid followed by 2 drops of a freshly prepared solution of 20% sodium nitrite. Stopper and shake vigorously for at least 10 sec. Allow to stand for 5 min. and examine the benzene layer. A strong yellow color indicates phenolic resin.

NOTE.—2,6-dichloroquinone-4-chlorimide may be used instead of the dibromo reagent.

**Styrene.**—There is no standard method for styrenated materials, but the test given below<sup>25</sup> has been found to be useful by the authors.

**Procedure.**—Place a few milligrams of the binder in a micro test tube, add four drops of fuming nitric acid (sp. gr. 1.5), and take to dryness by heating in a flame. The heating should start at the middle of the test tube and progress downward.

Continue by following the directions given under the Phenolic (Gibbs) Procedure above.

**Urea.**—No standard method for the detection of urea resins is available. However, at least three methods have appeared in the literature. In each of these methods the resin is hydrolyzed with acid to release urea which is then reacted with a reagent. In one method xanthidrol is used to form a precipitate of di-xanthyl urea;<sup>26</sup> in another, aniline, benzylamine, or *beta*-phenylethylamine is used

<sup>24</sup> Kappelmeier, C. P. A., op. cit., p. 26.

<sup>25</sup> Feigl, F., *Modern Plastics* 37(9), 151, 1960.

<sup>26</sup> Kappelmeier, C. P. A., op. cit., p. 167.



is a precipitant \* in the third method *p*-dimethylaminobenzaldehyde reagent forms a blue reaction product with urea<sup>28</sup> The third method is given below because it has been used by the authors and because both urea and melamine can be detected simultaneously

**Procedure**—Place 2 to 5 drops of the vehicle into a 50 ml round bottom flask having a standard 24/40 ground joint Add 10 ml of acetic acid acetic anhydride solution (3 volumes of acid to 10 volumes of anhydride) and a bumping stone such as a Berl saddle Then add 0.015 g of *p*-dimethylaminobenzaldehyde powder and attach an air condenser Heat the flask with an electric heater and increase the temperature until the contents reflux and vapors condense in the lower few inches of the condenser Continue the refluxing for 10 min

The appearance of a blue or blue green color in the flask is a positive test for urea resin In the absence of urea the test mixture develops a yellow color on refluxing If the urea content is very low the yellow color of the blank may be visible with the blue resulting in a green color

**Melamine** Several methods for detecting melamine have appeared in the literature but none of these is considered standard<sup>5 28 29</sup> The method of Swann and Esposito<sup>28</sup> is given below because it can be carried out simultaneously with the above urea test A second method by Feigl and Anger<sup>5</sup> is given as a confirmatory test

**Swann Procedure** Perform the urea test as given above being sure to weigh exactly 0.015 g of *p*-dimethylaminobenzaldehyde

If melamine is present an insoluble white residue collects in the condenser at the point of condensation and becomes more visible after the flask has cooled

**Feigl Procedure**—Place a few milligrams of the binder in a micro test tube and add a few drops of hydrochloric acid Heat the mixture gradually to 190 to 200 C in a glycerol bath until the vapors no longer turn Congo paper blue Cool the residue and add about 30 mg of thiosulfate Cover the mouth of the tube with a disk of Congo paper moistened with 3% hydrogen peroxide Now heat the tube to 160°C in a glycerol bath

If melamine resin is present a blue stain appears on the paper

**Rosin**—There are two standard qualitative tests for rosin the Liebermann Storch test and the Halphen Hicks test<sup>2</sup> The former is more reliable and is given below

**Procedure**—Place 0.1 to 0.2 g of the binder in a test tube (2.5 x 15 cm) and add about 15 ml of acetic anhydride Heat on a steam bath to effect solution cool and filter through paper (NOTE 1) Transfer a few drops of the filtrate to a white porcelain crucible cover (NOTE 2), and place a drop of sulfuric acid (3.7 ml of concentrated sulfuric acid (sp gr 1.84) to 34.7 ml of water) along side the filtrate Incline the cover in such a manner that the acid will slowly mix with the filtrate

If rosin is present a characteristic fugitive violet color develops immediately A pink or brown coloration should be ignored A control sample containing rosin should be run simultaneously

The characteristic color is due to reaction with the abietic type diene acids present in natural rosin Consequently any reactions which alter the double bond system of these acids interfere with color formation Thus rosin which has been

\* Kappelmeier C P A op cit p 176

<sup>28</sup> Swann M H and Esposito G C Anal Chem 30, 107 1958

<sup>29</sup> Kappelmeier C P A op cit pp 166 and 178

cooked into oils may not give a positive test. Also modifying reactions such as hydrogenation, disproportionation, polymerization, and adduct formation, when carried to completion, result in products which do not give a positive test. However, these reactions seldom are carried to completion in commercial products.<sup>30</sup>

NOTES.—1. Whatman No. 40 or equivalent is satisfactory.

2. Porcelain spot plate may be used instead.

**Methacrylates.**—There are no qualitative tests for methacrylate polymers which are regarded as standard. The procedure given below has been found to be useful by the authors.<sup>20</sup>

**Procedure.**—Place about 0.5 g. of binder in a 15 x 125-mm. test tube and pyrolyze by heating in a Bunsen flame, protecting against the escape of vapors by covering the mouth of the tube with a piece of filter paper held in place by a test tube clamp. To the drops of condensed pyrolyzate in the test tube, add a few milliliters of concentrated nitric acid (sp. gr. 1.40) and heat gently over the flame. (The solution may turn yellow.) Cool, and dilute with water to half the volume of the test tube. Add a few drops of a 10% sodium nitrite solution.

The immediate appearance of a blue color is a positive test for methacrylate. The blue color, but not the yellow, can be extracted by chloroform to intensify the color.

**Chlorinated Rubber.**—The reaction of sodium thiosulfate with terminal  $-\text{CH}_2\text{Cl}$  and  $-\text{CHCl}_2$  groups to form sulfur dioxide has been used to differentiate between chlorinated rubber and synthetic chloroprene rubber.<sup>25</sup>

**Procedure.**—Place a small piece of binder in a 15 x 125-mm. test tube and add about 0.5 g. of sodium thiosulfate. Then place the tube and contents into a glycerol bath which has been preheated to 80 to 100°C. and gradually raise the temperature. After the thiosulfate has been dehydrated at about 150°C., cover the mouth of the test tube with a piece of Congo paper moistened with 3% hydrogen peroxide and bring the bath to 170° to 180°C.

The indicator paper turns blue if resins containing terminal  $-\text{CHCl}_2$  or  $-\text{CH}_2\text{Cl}$  groups are present. Chlorinated natural rubber gives a positive test whereas synthetic chloroprene rubber gives a negative test.

### CHEMICAL AND SOLUBILITY CLASSIFICATION TESTS

Certain chemical procedures which yield a quantitative result, such as saponification number and hydroxyl number, have been used to classify binder materials.<sup>5, 10, 19</sup> In the opinion of the authors these procedures are of limited value when applied to a completely unknown binder. However, once it has been established by infrared or other methods that a single type of binder material is present, these procedures may be used to further characterize the binder. For example, once it is known that the binder is an oil, the saponification number helps to establish which oil. Because these chemical procedures are most useful in the quantitative analysis of the identified binder, they are given in the sections on the Analysis of the Vehicle, under Oils and Alkyls.

Solubility tests also have been used to classify binders into types.<sup>5, 10</sup> In fact, Shaw<sup>19</sup> and others have presented a comprehensive identification scheme based on solubility and qualitative tests. The chief disadvantage of a solubility scheme for identification purposes is due to the fact that most resins used in coatings gen-

<sup>30</sup> Mano, E. B., Anal. Chem. 32, 291, 1960.

erally vary in molecular weight and hence in solubility. In view of the infrared method and the newer spot tests the authors feel that the general solubility scheme is the least reliable. On the other hand when the type of binder present is known and when it has been freed of plasticizer solubility differences can be used for identification as well as for separation. An interesting example of the latter case involves the cellulose derivatives.<sup>31</sup> Information on the general solubility of resins can be found in several references.<sup>30, 31, 32</sup>

### IDENTIFICATION OF PLASTICIZERS

As stated earlier (page 1627) the binder of a lacquer formulation almost always contains a plasticizer in addition to the polymeric film former. Many binders found in latex formulations also contain plasticizers. Unfortunately there are no standard or generally accepted methods for separating and identifying plasticizers. Once the polymer present in the binder has been identified (or at least tentatively identified by the methods given above (under Identification of Polymers, Resins and Oils) the plasticizer may be isolated according to the procedures given under the heading of the polymer in the following sections on Analysis of the Vehicle.

There are two general ways of separating the plasticizer and the polymer portions of a binder: a solvent-nonsolvent method and a Soxhlet extraction method. The solvent-nonsolvent method is probably the most widely used and involves the dissolution of the binder in a suitable solvent followed by precipitation of the polymer by the addition of a nonsolvent. The polymer-nonsolvent must be a solvent for the plasticizer and must be miscible with the solvent used to dissolve the binder. The Soxhlet procedure involves extraction of a finely divided sample of binder with ether or some other plasticizer solvent. Hanson<sup>31</sup> has described an interesting Soxhlet type procedure in which the total formulation (including pigment and thinner) is dispersed on silt, the thinner evaporated, and then the powdered nonvolatile matter placed in a Soxhlet thimble and successively extracted with various solvents. In the case of a cellulose nitrate formulation petroleum ether may be the first extraction solvent used to remove simple plasticizers. Benzene might then be used to remove certain resins. This may be followed by acetone to remove the cellulose nitrate, leaving the pigment dispersed on the sodium chloride. Finally the pigment can be recovered by extracting the salt with water.

Once the plasticizer portion of the binder has been isolated the best way to identify the type of plasticizer present is by means of its infrared absorption spectrum. Consequently a scheme for the identification of plasticizers based on the most significant absorption bands is given in Table 37.4. The spectra of four of the most commonly encountered plasticizers also are included in the section on infrared spectra (also see Table 37.2). Other reference spectra of plasticizers may be found in the literature: seventy-nine in reference<sup>33</sup>, ten in reference<sup>34</sup>, and nineteen in reference<sup>35</sup>. The latter spectra are those of plasticizers encountered in poly(vinyl chloride) formulations.

Although the type of plasticizer may quickly be determined by infrared methods it is difficult to establish exactly which plasticizer is present by infrared alone. If

<sup>31</sup> Hanson, N. W. J. Oil and Colour Chemists' Assoc. 41, 242 (1958).

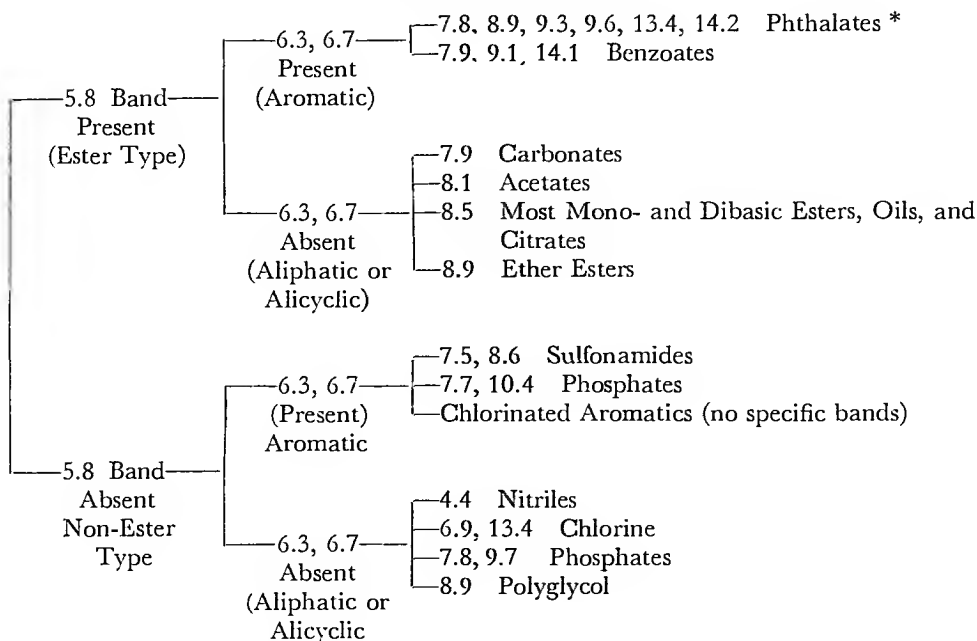
<sup>32</sup> Mattiello, J. J. Protective and Decorative Coatings, vol. 1, p. 112. John Wiley and Sons, 1946.

<sup>33</sup> Kendall, D., Hampton, R., Hausdorff, H., and Prister, F. Appl. Spectroscopy 7, 179 (1953).

<sup>34</sup> Hashim, J., Soppet, W., and Willis, H. A. J. Appl. Chem. 1, 112 (1951).

TABLE 37-4. SCHEME FOR IDENTIFICATION OF PLASTICIZERS BASED ON INFRARED ABSORPTION BANDS

(Wavelength in microns)



\* Specific phthalates can further be distinguished by comparison of the 8.3 to 12.2 micron region as shown in references. 6, 30, 33

the plasticizer is shown to be a phthalate ester type, it may be injected into a gas chromatograph for further identification. Phthalates from dimethyl phthalate up to and including dioctyl phthalate have been separated on a silicone grease-Celite column at 206°C. with a helium flow rate of 124 ml./min. and identified from their retention times.<sup>35</sup> If higher phthalate esters or phthalate alkyds are suspected, the plasticizer should be saponified and the alcohol and/or fatty acids portions identified by the methods given under the analysis of alkyds (page 1649).

The chemical qualitative and spot test methods given above for the polymer portion of the binder can be used for the plasticizer portion as well. In addition to the elemental tests listed in Table 37-3, a qualitative test for phosphorus is useful since tricresyl phosphate is a very common plasticizer.

## ANALYSIS OF THE VEHICLE

### GENERAL

The analysis of the vehicle portion of a pigmented coating (or a clear coating) generally is aimed at characterizing the binder or nonvolatile portion of the vehicle, and perhaps it may seem more logical to have entitled this section The

<sup>35</sup> Dal Nogare, S. and Safranski, L. W., Anal. Chem. 30, 894, 1958.

**Analysis of the Binder** However even though only the composition of the binder is desired its analysis is carried out via procedures applied to the total vehicle. For this reason and to provide a starting place for the analysis of clear coatings in the analytical scheme of this chapter this section was labeled as shown above. Of course before the procedures in this section are utilized the binder must be identified by the methods given in the section on the Identification of Binder.

As indicated above (page 1621) the separation of vehicle from pigment is almost never quantitative. The vehicle may contain soluble reaction products of the pigment with the binder as well as additives such as driers. Methods for determining the metal content of vehicles are discussed in reference <sup>36</sup>. The authors have found that the metal content of an acid extract of a vehicle or drier solution can be determined rapidly and accurately by an EDTA (ethylenedinitrilo) tetraacetate titration <sup>37 38 39 40</sup>.

When an analysis of the volatile portion (thinner) of a paint or clear coating is desired it should be separated as given in the section on Isolation of Thinner (page 1623) and treated according to the procedures given in the sections on Identification and Analysis of the Thinner (page 1703).

### NONVOLATILE VEHICLE CONTENT

**General**—The nonvolatile content of the vehicle (the concentration of the binder present) must be known to calculate the composition of the binder when the analysis is carried out via the total vehicle. Consequently the first step in the analysis of the vehicle is the determination of the per cent nonvolatile vehicle (%NVV) by evaporating the volatile thinner in an oven under specified conditions. The %NVV may be calculated from the %NVM of the total paint and the per cent pigment when these are known as shown in the section on Calculation of Binder or Pigment Contents (page 1625). However if the sample is a clear coating or if the %NVM and per cent pigment are not known then the %NVV must be determined. In order to obtain the true nonvolatile content of a resin solution no thinner must be left in the film formed upon release of the thinner and the binder must not gain or lose weight through chemical reactions such as oxidation or degradation. To achieve reproducible results the amount of sample, the temperature and the time of heating must be carefully controlled. The use of a vacuum oven is also desirable for those resins and oils which may gain weight through oxidation. Unfortunately there actually is no true per cent nonvolatile vehicle content for many resin solutions because the nonvolatile content found depends upon the procedure used. ASTM Committee D1 has tested several procedures for determining the per cent nonvolatile content of resin solutions and to date has found only one which gives accurate and precise results for a wide variety of resin solutions; the procedure is known as the foil method.

In the foil method a weighed sample of resin solution is spread into a thin film between two sheets (or one sheet folded in half) of aluminum or tin foil. The coated foil sheets are separated and then dried. The weight of residue is determined and the nonvolatile content is calculated. The method is unique in that it provides for drying of a very thin film of resin thus minimizing chances for vola-

<sup>36</sup> Kappelmeier C P A op cit p 225

<sup>37</sup> Hirm C F and Lucchesi C A Anal Chem 31, 1417 1959

<sup>38</sup> Lucchesi C A and Hirm C F Anal Chem 30 1817 1958

<sup>39</sup> Lucchesi C A and Hirm C F Anal Chem 32, 1191 1960

<sup>40</sup> Lucchesi C A Stearns J A and Hirm C F Chemist Analyst 48 9 1959

tiles to be trapped and held during the heating operation. In the newly revised A.S.T.M. Method D1259-61<sup>1,41</sup> two procedures are given, method *A* for non-heat-reactive resins and method *B* for heat-reactive resins and for resins which release thinner slowly. The non-heat-reactive resins, such as alkyds and rosin esters, remain stable and release the thinner under the conditions of the test. Heat-reactive resins, such as the formaldehyde reaction products of urea, melamine, and phenols, undergo condensation or other reactions or both under the influence of heat. Epoxides are examples of resins which release thinner slowly. The two methods differ primarily in the drying times and types of ovens used. In method *A* either a gravity-convection or a forced-ventilation oven and a 30-minute heating period at 105°C. are used. In method *B* a forced-ventilation oven and a 2-hour heating period at 105°C. are used.

In spite of the demonstrated superior accuracy and precision of the foil method, it is not used routinely in most laboratories because it is very time-consuming. Most laboratories, including the authors' laboratory, use the dish method (page 1618) for routine determinations and use the foil method to settle disagreements which might arise between two laboratories. An abstract of the foil method is given below.

**Procedure for Foil Method.**—Weigh to the nearest 0.1 mg. a 6 x 12-in. piece of aluminum or tin foil and fold in half. Place 0.9 to 1.1 g. of resin solution on the center of one-half of the tared foil. Fold the foil over the resin sample and press the sandwich between glass plates to distribute the resin over the foil in a thin film.

Open the foil and place it into the appropriate oven and heat for either 0.5 or 2 hours, depending upon whether the resin should be treated by method *A* or method *B*.

## ANALYSIS OF DRYING OILS

### GENERAL

An oil is a triglyceride which, in turn, is an ester of glycerol and fatty acids. A triglyceride may contain one single kind of fatty acid or may contain as many as three kinds of fatty acids. Most oils are mixtures of triglycerides, and consequently, the analysis of an oil means establishing which fatty acids are present and how much of each is present. Strictly, it might also mean determining the nature and amounts of other minor or trace components which are present even in refined natural oils. Fortunately, the commonly used drying oils contain large amounts of one or two very characteristic fatty acids, and it is usually sufficient to determine only the characteristic fatty acids in an analysis. When a single oil is present, an "analysis" actually amounts to an identification of the oil. When two or more oils are present, determination of the relative amounts of the characteristic fatty acids of each oil provides an approximate analysis which is usually sufficiently accurate for most purposes. The approximate compositions of the raw oils commonly encountered in coatings are given in Table 37-5. Those fatty acids present to the extent of 50% or more are considered the characteristic acid for that particular oil. The oils listed may be given various treatments, such as heating, blowing with air, and reaction with unsaturated compounds, which change their composition and make them more suitable for certain applications.

<sup>41</sup> American Society for Testing and Materials, Philadelphia, Pa., A.S.T.M. Standards, Part 8, 1961.

TABLE 37 5 FATTY ACID COMPOSITION OF SOME COMMON OILS %

<i>Fatty Acid</i>	<i>Coconut</i>	<i>Soybean</i>	<i>Linseed</i>	<i>Tung</i>	<i>Opticica</i>	<i>Castor</i>
<b>Saturated Acids</b>						
Less than 12 carbons	15	—	—	—	—	—
Lauric	50	—	—	—	—	—
More than 12 carbons	25	10	10	5	10	5
<b>Unsaturated Acids</b>						
Oleic	5	30	25	10	5	5
Linoleic	5	55	15	5	?	?
Linolenic	—	5	50	—	—	—
Eleostearic	—	—	—	80	—	—
Licanic	—	—	—	—	80	—
Ricinoleic	—	—	—	—	—	90

At the present time there are standard tests for determining some chemical properties of oils such as poly unsaturation<sup>4</sup> iodine number saponification number acid number and hydroxyl number<sup>1</sup> but there are no methods for the analysis of oils which are regarded as standard. The methods presented in this section are those found to be useful by the authors. Of the three methods presented only the gas chromatographic method truly involves analysis of the oil. The others involve the identification of characteristic fatty acids present in the oils.

#### INFRARED METHOD

As indicated in Table 37 1 the infrared absorption bands of oils at 5.8 (actually 5.75) 6.85 8.1 and 8.6 microns help to distinguish the oils from other binder materials. In addition most oils have a weak absorption band at 13.8 microns due to the presence of  $-\text{CH}_2-$  groups in the fatty acid chain. Oils containing *cis* unsaturation exhibit a rather broad band between 13 and 15 microns and the intensity of absorption in this region may be utilized in differentiating relatively highly unsaturated oils such as soybean and linseed from slightly unsaturated oils such as coconut.

Several oils exhibit very characteristic absorption bands which may be used to distinguish them from other oils. Tung and opticica oils have rather specific absorption bands at 10.1 (strong) and 10.3 (weak) microns which are due to the conjugated triene systems they contain. Opticica oil also has a characteristic band at 5.83 microns due to the ketone group it contains. Dehydrated castor oil has characteristic bands at 10.2 10.35 and 10.6 microns. Raw castor oil has a characteristic band at 3.0 microns due to the hydroxyl group it contains. Spectra of raw linseed opticica tung and dehydrated castor oil are given as numbers 8 9 10 and 11 in the section on Infrared Spectra (page 1708) of this chapter. Spectra of other oils may be found in references<sup>6 14</sup>.

Some of the treatments that oils may undergo alter the infrared spectrum of the raw oil. Heat bodying of oils such as linseed results in *trans* unsaturation which in turn results in rather strong absorption at 10.3 microns. Blown oils usually absorb at about 3.0 microns due to the formation of hydroxyl groups. The blown oils also usually exhibit some absorption at 10.3 microns due to *trans* unsaturation.

<sup>42</sup> American Oil Chemists Society, Chicago, Ill. Official and Tentative Methods of American Oil Chemists Society, Method Cd 7 48.

Modification of oils with styrene results in strong absorption at 13.2 to 13.4 microns and at 14.3 microns. Modification of oils with vinyl toluene results in strong absorption at 12.3, 12.8, and 14.3 microns. An idea of what the bands due to styrene and vinyl toluene look like can be obtained from the spectra of styrenated and vinyl toluenated alkyds, spectra 2 and 3 in the section on Infrared Spectra.

#### IDENTIFICATION BY PHYSICAL AND CHEMICAL TESTS

Most oils can be identified by means of refractive index, iodine number, and saponification number. Values of refractive index, iodine number, and saponification number of several oils are listed in Table 37-6.

TABLE 37-6. SOME PHYSICAL AND CHEMICAL CHARACTERISTICS OF OILS

<i>Oil</i>	<i>Refractive Index at 25°C. (approximate)</i>	<i>Iodine Number</i>	<i>Saponification Number</i>
Linseed	1.479	155-205	188-196
Soya	1.475	125-135	189-195
Dehydrated Castor	1.483	135-141	192-196
Tung	1.518	160-175	189-195
Oiticica	1.515	140-160	186-193
Cottonseed	1.475	99-113	189-198
Coconut	1.454	7-11	250-264

As oils, such as linseed or soya, are polymerized (heated or blown), the iodine number decreases and the refractive index increases. Consequently, the combination of a low iodine number plus a high refractive index indicates the oil has been heat-bodied or blown. Modification with aromatic vinyls such as styrene or vinyl toluene results in a higher refractive index, lower iodine number and lower saponification number. Reaction with unsaturated dicarboxylic acid materials such as maleic anhydride results in a higher saponification number and a lower iodine number. A.S.T.M. Method D555-58 contains procedures for determining refractive index, iodine number, and saponification number of drying oils and fatty acids. Abstracts of these methods are given below.

**Refractive Index.**—The refractive index of the oil or the nonvolatile portion of the vehicle at 25°C. may be determined by means of a properly standardized Abbe refractometer or any other equally accurate instrument. The procedure recommended by the manufacturer for making measurements and cleaning the prisms should be followed.

**Iodine Number.**—Iodine number is a measure of the unsaturation of fats and oils and is expressed in terms of the number of centigrams of iodine absorbed per gram of sample (percentage by weight of iodine absorbed). When the iodine number of oils having conjugated systems is determined, the result is not a measure of total unsaturation, but rather is an empirical figure indicative of the amount of unsaturation present. Reproducible results are obtained which afford a comparison of total unsaturation.

**Procedure.**—Filter the vehicle containing the oil through filter paper to remove any solid impurities and the last traces of moisture. The sample must be absolutely dry. All glassware used in this test must be completely dry. Sample drying oils of high viscosity should not be filtered.



Place in a 500 ml iodine flask to which has been added 20 ml of carbon tetrachloride, a weight of sample such that there will be an excess of Wijs' solution of  $125 \pm 25\%$  of the amount absorbed for normal oils and  $125 \pm 10\%$  for the conjugated oils. Sample weights meeting this requirement are given in Table 37-7.

TABLE 37-7. SAMPLE SIZE FOR IODINE NUMBER DETERMINATION

Iodine Number	Sample Size (grams)	
	Normal Oils	Conjugated Oils
80	0.3175 to 0.3969	0.3377 to 0.3691
90	0.2822 to 0.3528	0.3002 to 0.3281
100	0.2540 to 0.3175	0.2702 to 0.2953
110	0.2309 to 0.2886	0.2456 to 0.2684
120	0.2117 to 0.2646	0.2252 to 0.2461
130	0.1954 to 0.2442	0.2078 to 0.2271
140	0.1814 to 0.2268	0.1930 to 0.2109
150	0.1693 to 0.2116	0.1801 to 0.1969
160	0.1587 to 0.1984	0.1689 to 0.1846
170	0.1494 to 0.1868	0.1589 to 0.1737
180	0.1411 to 0.1764	0.1501 to 0.1640
190	0.1337 to 0.1671	0.1422 to 0.1554
200	0.1270 to 0.1587	0.1351 to 0.1476
210	0.1210 to 0.1547	0.1287 to 0.1406
220	0.1155 to 0.1443	0.1228 to 0.1374

Pipet 25 ml of Wijs' solution (see NOTE) into the flask containing the sample and also into each of at least two additional flasks to be carried through as blanks. Stopper the flasks, and swirl the flask containing the sample to ensure intimate mixture. Store the flasks in a dark place for 1 hr at a temperature of  $25 \pm 5^\circ\text{C}$ . For conjugated oils, such as tung oil or dehydrated castor oil, allow the absorption to proceed for 1 hr at  $25 \pm 1^\circ\text{C}$ .

Remove the flasks from storage and add 20 ml of potassium iodide solution (150 g per liter) and 100 ml of water. Titrate with 0.1 *N* sodium thiosulfate solution (24.8 g per liter), adding it gradually and with constant and vigorous shaking. Continue the titration until the yellow color has almost disappeared. Add 1 to 2 ml of starch indicator solution and continue the titration until the blue color has just disappeared.

Calculation —

$$\text{Iodine Number} = \frac{(B - A) \times N \times 12.69}{W \times S}$$

where *A* = ml of  $\text{Na}_2\text{S}_2\text{O}_3$  solution required for titration of the sample,

*B* = ml of  $\text{Na}_2\text{S}_2\text{O}_3$  solution required for titration of the blank,

*N* = normality of the  $\text{Na}_2\text{S}_2\text{O}_3$  solution,

*W* = weight of sample, and

*S* = fractional nonvolatile content of sample

NOTE—Wijs' solution obtained from Fisher Scientific Company has been found to be satisfactory. It may be prepared by a method given on page 1439.

**Saponification Number.**—Saponification number is a measure of the alkali reactive groups in fats and oils and is expressed as the number of milligrams of potassium hydroxide that react with 1 g. of sample.

**Procedure.**—Prepare an alcoholic potassium hydroxide solution by placing 5 to 10 g. of potassium hydroxide in a 2-liter flask and add 1 to 1.5 liters of ethyl alcohol (95%) or denatured alcohol conforming to USSD Formula 30 or 3A of the United States Bureau of Internal Revenue. Boil on a water bath under a reflux condenser for 30 to 60 minutes. Distill and collect the alcohol. Dissolve 40 g. of potassium hydroxide in 1 liter of the distilled alcohol, keeping the temperature below 15.5°C. while the alkali is being dissolved. This solution should remain clear.

Transfer 2.0 to 2.5 g. of the sample, weighed to the nearest 0.001 g., to an Erlenmeyer flask. Add 25 ml. of the alcoholic potassium hydroxide solution to the sample and to one or more additional flasks to be carried through as blanks. Place a condenser loop inside the neck of each flask (NOTE 1). Heat on a steam bath for 1 hr. (NOTE 2).

Cool the solution, add phenolphthalein indicator, and titrate with 0.5 *N* sulfuric acid or hydrochloric acid until the pink color has just disappeared (NOTE 3).

**Calculation.**—

$$\text{Saponification Number} = \frac{(B - A) \times N \times 56.1}{W \times S}$$

where *A* = ml. of acid required for titration of the sample,

*B* = ml. of acid required for titration of the blank,

*N* = normality of acid,

*W* = grams of sample, and

*S* = fractional nonvolatile content of sample.

**NOTES.**—1. Suitable condenser loops are shown in Figures 1 and 2 of A.S.T.M. Method D305-51.

2. Certain synthetic oils are not completely saponified in 1 hr. Run samples of chemically modified drying oils in duplicate, using 1- and 2-hr. heating periods to establish completeness of saponification. If the 2-hr. heating period gives appreciably higher results than the 1-hr. run, additional 4- and 6-hr. determinations should be made to establish the time required for complete reaction.

3. A "masked phenolphthalein indicator" may be used with off-color materials. It may be prepared by dissolving 1.6 g. of phenolphthalein and 2.7 g. of methylene blue in 500 ml. of denatured alcohol (USSD Formula 30 or 3A). The pH is adjusted with sodium hydroxide or potassium hydroxide solution so that the greenish-blue color is faintly tinged with purple. Color change is from green to purple when going from acid to alkali.

### GAS CHROMATOGRAPHY

The simplest and most rapid way to identify and to determine the fatty acids of an oil is by gas-liquid-partition chromatography.<sup>43,44</sup> By this relatively new method it is possible to separate the methyl esters of the fatty acids found in dry-

<sup>43</sup> Dal Nogate, S. and Safhanski, L. W., "Gas Chromatography" in Organic Analysis, ed. Mitchell, Kolthoff, Proskauer, and Weissberger, vol. 4, p. 91, Interscience Publishers, New York, N. Y., 1960.

<sup>44</sup> James, A. T., "Qualitative and Quantitative Determination of Fatty Acids by Gas-Liquid Chromatography" in Methods of Biochemical Analysis, ed. D. Glick, vol. 8, p. 1, Interscience Publishers, New York, N. Y., 1954.

ing oils and to measure the relative amounts of each fatty acid present. It is also possible to determine roughly the amount of polymerization which has occurred in blown and heat bodied oils<sup>45</sup>

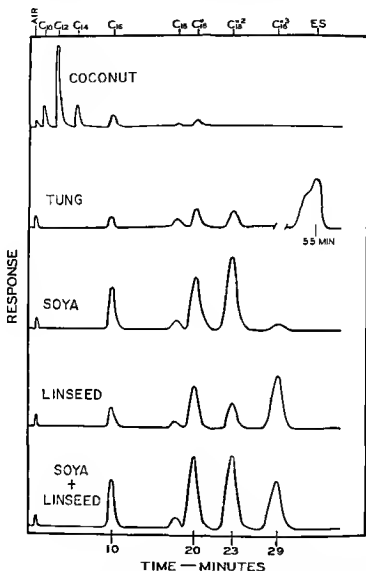


FIG. 37.3. Chromatograms of the Fatty Acid Methyl Esters of Some Oils. C<sub>10</sub> Represents Capric Acid, C<sub>12</sub> Lauric Acid, C<sub>14</sub> Myristic, C<sub>16</sub> Palmitic, C<sub>18</sub> Stearic, C<sub>18</sub><sup>2</sup>, Oleic, C<sub>18</sub><sup>3</sup> Linoleic, C<sub>18</sub><sup>3</sup> Linolenic, and ES for Eleostearic Isomers.

The gas chromatograms of the fatty acid methyl esters of several oils are presented in Fig. 37.3. The areas under the peaks are proportional to the concentration of the acid represented by the peak, and the concentration of a particular

<sup>45</sup> Ziembinski, W. L., Jr., Moseley, W. V., Jr., and Bricker, R. C., National Meeting of the American Chemical Society, Organic Coatings and Plastic Chemistry Division, New York, Sept. 1960, Offic. Dig. Federation Soc. Paint Technology 33, May 1961.

fatty acid may be approximated by dividing the area under its peak by the total area under all the peaks. Visual comparison of the chromatogram of an unknown with that of a known is usually sufficient to identify the oil from which the fatty acids were derived. The procedure used to obtain the chromatograms is given below.

**Procedure.**—Saponify a sample of an oil or oil-modified binder large enough to yield about 250 mg. of total fatty acids with about 150 ml. of 4% ethanolic potassium hydroxide for 1 hour.

Extract the oil acids by the procedure given for the filtrate from the phthalic anhydride determination in alkyds as described in the Procedure (page 1652). Evaporate most of the ether from the fatty acids and add 2 to 3 ml. of a boron trifluoride-methanol solution (120 g. of boron trifluoride per liter of methanol) (NOTE 1). Heat on a steam bath for about 3 minutes. Then transfer a representative sample of the methanolic solution to a 250-ml. separatory funnel containing about 60 ml. of water. Extract the methyl esters with 50 ml. of ether and then evaporate the ether on a steam bath. Take up 3 microliters of the methyl esters with a microsyringe and inject the contents into a gas chromatograph (NOTE 2).

Use a diethylene glycol succinate-Chromosorb column maintained at 225°C. and a helium flow rate of 85 ml. per minute.

NOTES.—1. A procedure for preparing the boron trifluoride-methanol solution can be found in reference <sup>46</sup>.

2. The F and M Model 202 gas chromatograph has been found to be satisfactory.

## ANALYSIS OF ALKYD RESINS

### GENERAL

An alkyd resin may be defined as a polyester of a polyhydric alcohol and a dicarboxylic acid. Alkyd resins used as varnishes or paint vehicles are modified with oil or fatty acids. By far the most commonly encountered dicarboxylic acid is *ortho*-phthalic acid. Isophthalic, maleic and fumaric acid also are used extensively. Succinic, adipic, azelaic or sebacic acids may be found in alkyd resins. The polyhydric alcohols or polyols used extensively are glycerine, pentaerythritol and ethylene glycol. The oils and fatty acids most commonly used in alkyd resins are soybean, linseed, coconut, castor, dehydrated castor, and fish.

The analysis of an alkyd resin involves first breaking down the resin into its three basic monomeric fractions (a dicarboxylic acid fraction, a fatty acid fraction, and a polyhydric alcohol fraction) and then analyzing each fraction. This is accomplished by first saponifying the resin with ethanolic potassium hydroxide solution. Insoluble potassium salts of the dicarboxylic acids are formed and removed by filtration. The filtrate is then extracted with ether to remove unsaponifiable material. The water layer remaining after extraction of the unsaponifiable matter is then acidified, and the fatty acids are extracted with ether. The remaining water solution containing the polyhydric alcohols is passed through ion exchange resins to remove all ions and is then carefully evaporated and dried to recover the polyhydric alcohols.

Alkyd resins are formulated and manufactured in such a way that the resin contains acid and hydroxyl groups and the characteristics of the resin depend partially upon the amount of each of these groups. Consequently, the amount of acid

<sup>46</sup> Metcalfe, L. D. and Schmitz, A. A., *Anal. Chem.* **33**, 363, 1961.

and hydroxyl groups must be determined for complete characterization and quantitative analysis of the resin

#### DICARBOXYLIC ACIDS FRACTION (PHTHALIC ANHYDRIDE)

Standard methods are available for determining the phthalic content (as phthalic anhydride) of alkyls and these methods fall roughly into two types. The first type provides for the determination of phthalic anhydride in alkyls which contain only phthalic as the dicarboxylic acid; the second type provides for the determination of phthalic anhydride in alkyls which also contain other dicarboxylic acids. ASTM Method D563-52 is an example of the first type and is based on the pioneering methods of Kappelmeier.<sup>1-6</sup> ASTM Methods D1306-56 (gravimetric) and D1307-56 (spectrophotometric) are examples of the second type. Recently ASTM has made available a method D1651-61, for the determination of the phthalic acid isomers and benzoic acid in alkyls which contain only the four acids.

Although not a standard method, the authors have found a method reported by Swann<sup>47</sup> for the determination of dicarboxylic acids other than *ortho* phthalic to be very useful.<sup>11-48</sup> This method is applicable to alkyls containing maleic, fumaric, succinic, adipic, or sebacic acids in addition to *ortho* phthalic acid. In the method all the dicarboxylic acids present are obtained as the dipotassium salts by a modified Kappelmeier saponification procedure. The total dicarboxylic acid fraction is redissolved and each acid component is determined by selective precipitation or bromination.

The nature of the dicarboxylic acids present in the alkyl and an estimate of their relative amounts can be obtained from the infrared absorption spectrum of the total alkyl as is indicated in the section on the Identification of Polymers, Resins and Oils (page 1628).<sup>14-49</sup> When more information is desired about the identity of the dicarboxylic acids in the alkyl, it may be obtained from the infrared spectrum of the dicarboxylic acid fraction.<sup>50-52</sup>

An abstract of ASTM Method D563-52 for the determination of the phthalic anhydride content of alkyl resins containing no other dicarboxylic acids and no modifying resins such as urea, melamine, or phenolics, is given below.

**Procedure**—Weigh by difference a sample of vehicle or resin solution sufficient to yield from 0.8 to 1.2 g. of dipotassium phthalate monoalcoholate into a 500 ml. Erlenmeyer flask with a ground glass joint. Add 150 ml. of benzene, warming slightly on a steam bath if necessary, to effect solution. Add 60 ml. of anhydrous ethyl alcoholic potassium hydroxide solution containing 66 g. of potassium hydroxide per liter of alcohol. Attach air condenser to the flask and place flask in a water bath to a depth about equal to that of the contents of the flask. Warm the bath, maintaining a temperature of 40°C. for 1 hour, and then gradually raise the temperature until the alcoholic solution boils gently. Reflux for 1.5 hours.

Remove the flask from the bath and wash down the inside of the condenser with a few milliliters of a solution consisting of one volume of absolute ethyl alcohol and three volumes of benzene. Remove the condenser, cap the flask, and cool.

When cool, filter with vacuum immediately and as rapidly as possible through a tared fritted glass crucible using the alcohol-benzene solution for transferring the

<sup>47</sup> Swann, M. H., *Anal. Chem.* **21**, 1448-53, 1949.

<sup>48</sup> Kappelmeier, C. P. A. op. cit. p. 570.

<sup>49</sup> Adams, M. L. and Swann, M. H., *Anal. Chem.* **30**, 1322, 1958.

<sup>50</sup> Stafford, R. W., Shay, J. F., and France, R. J., *Anal. Chem.* **26**, 656, 1954.

<sup>51</sup> Childers, E. and Strubers, G. W., *Anal. Chem.* **27**, 737, 1955.

precipitate and washing the reaction flask. Wash the precipitate with successive portions of the alcohol-benzene solution until a few milliliters of the washings collected in a second suction are no longer alkaline to phenolphthalein. Do not allow air to be drawn through the crystals, as they are hygroscopic. Finally pour 25 ml. of ether into the crucible and draw through the precipitate with the aid of suction.

Wipe the outer surface of the crucible with a clean cloth and place in a gravity convection oven at 60°C. for 1 hour (NOTE 1). Cool to room temperature in a desiccator and weigh.

**Correction for Carbonates.**—Coprecipitation of potassium carbonate with the potassium phthalate alcoholate may be a source of error. If a correction for potassium carbonate is desired, dissolve the weighed precipitate in about 50 ml. of distilled water that has been neutralized to phenolphthalein, add 3 to 4 drops of phenolphthalein indicator, and if the solution is alkaline, titrate with 0.1 *N* hydrochloric acid.

**Calculation.**—The percentage of phthalate present in the alkyd is calculated as the anhydride because phthalic anhydride is the usual starting material in the manufacture of the resin.

$$\text{Phthalic Anhydride, \%} = \frac{(P - K) \times 0.5136 \times 100}{W \times S},$$

where *P* = grams of dipotassium phthalate monoalcoholate;

*K* = correction for potassium carbonate = 0.1382 *VN*, where

*V* = ml. of hydrochloric acid used for titration, and

*N* = normality of hydrochloric acid;

*W* = grams of vehicle or resin solution; and

*S* = fractional nonvolatile content of vehicle or resin solution.

**NOTES.**—1. The precipitate is the monoalcoholate,  $\text{C}_6\text{H}_4(\text{COOK})_2 \cdot (\text{C}_2\text{H}_5\text{OH})$ , and the alcohol of crystallization will be slowly driven off on prolonged heating. It is safe, however, to dry the alcoholate at temperatures up to 60°C. for as long as 1 hour. This behavior of the alcoholate has been made the basis of a method for determining the phthalic content of alkyd resins containing other dicarboxylic acids which do not form alcoholates. The procedure involves first drying the precipitate as above at 60°C. for 1 hour, weighing, and then heating the precipitate at 150°C. for about 3 hours to remove the alcohol of crystallization, reweighing, and noting the difference in weight. The percentage of phthalic anhydride in the alkyd is calculated as follows: per cent phthalic anhydride = difference in weight  $\times 3.217 \times 100 / W \times S$  where the symbols have the same meaning as above.

2. Data presented by Stafford, Shay, and Francel<sup>50</sup> indicate that the above A.S.T.M. procedure may be extended to the determination of maleic, fumaric, adipic, and sebacic acids when one of these comprises the sole acid component of the polyester.<sup>6,11</sup> Work in the authors' laboratory and other published work indicate that maleic and fumaric polyesters give high results for the dicarboxylic acid fraction due to the formation of ethoxysuccinate upon alcoholic saponification.<sup>5</sup>

### FATTY ACIDS FRACTION

The analysis of the fatty acids in an alkyd resin involves first separating the fatty acids fraction and then determining from which oil the fatty acids were derived.

**Separation of the Fatty Acids Fraction.**—The standard method for determining the total fatty acids content of an alkyd is A.S.T.M. Method D563-52. An abstract of this procedure applied to the filtrate remaining from the phthalic anhydride determination is given in the following Procedure.

absorption spectra of the fatty acids exhibit more overall absorption than those of the oils, but the bands characteristic of the oils are still observable in the spectra of the fatty acids. The presence of the carboxyl group in the free acid does obscure the ketone band of oiticica at 5.83 microns. The carboxyl group is also responsible for a stronger and broader absorption near 3.0 microns. The iodine number or saponification number of fatty acids is approximately five per cent higher than that of the corresponding oil. The refractive index of fatty acids is approximately 0.01 less than that of the corresponding oil. As with the oils, the individual fatty acids can be best separated and identified with the aid of gas chromatography.<sup>45</sup>

In addition to the chemical tests used as an aid in identifying an oil (as given in the section on Drying Oils, page 1645) two other tests are useful in identifying the fatty acids derived from an alkyd resin. These tests are the acid number, which is a measure of the average equivalent weight of the fatty acids fraction, and the hydroxyl number, which is important in characterizing fatty acids which contain a hydroxyl group.

**Acid Number.**—The acid number of the fatty acids fraction corresponds to the saponification number of the oil from which the fatty acids are derived (see Table 37-6, page 1645). The acid number is defined as the number of milligrams of potassium hydroxide required to neutralize the free acids in 1.0 g. of sample. An abstract of a procedure taken from A.S.T.M. Method D1639-61 for the determination of the acid number of organic coating materials is given below. Of course, the procedure is also applicable to the determination of the acid number of the fatty acids fraction.

**Procedure.**—Transfer to a 250-ml. Erlenmeyer flask the weight of sample prescribed in Table 37-8.

TABLE 37-8. SAMPLE SIZE FOR ACID NUMBER DETERMINATION

<i>Acid Number</i>	<i>Approximate Weight of Sample, g.</i>	<i>Accuracy of Weighing, plus or minus, g.</i>
0 to 5	20	0.05
5 to 15	10	0.05
15 to 30	5	0.05
30 to 100	2.5	0.001
100 and over	1.0	0.001

Add 100 ml. of a neutral benzene-alcohol mixture (1:1 by volume and neutralized to a faint but persistent pink color of phenolphthalein) to the sample and shake until solution is complete. Warming may be necessary for bodied oils.

Titrate with 0.1 *M* potassium hydroxide or sodium hydroxide solution, while shaking vigorously, to the first appearance of a persistent pink color of the same intensity as that of the neutral benzene-alcohol mixture. The color must persist for at least 30 seconds. In the case of off-color material (see directions for masked phenolphthalein indicator in NOTE 3 of method for saponification number (page 1647) the color should be observed in the alcohol layer above the sample after the sample has been allowed to settle. The sample usually will settle in a minute or less.

## Calculation —

$$\text{Acid Number} = \frac{A \times N \times 56.1}{W \times S}$$

where  $A$  = milliliters of potassium hydroxide or sodium hydroxide solution,  
 $N$  = normality of the potassium hydroxide or sodium hydroxide solution  
 $W$  = grams of sample used and  
 $S$  = fractional nonvolatile content of sample

**Hydroxyl Number**—The hydroxyl number of fatty acids is useful in detecting and determining the amount of castor fatty acids. The hydroxyl number of a sample is the number of milligrams of potassium hydroxide equivalent to the hydroxyl content of 1.0 g of the sample. The hydroxyl number of castor fatty acids is approximately 172. Other refined untreated fatty acids usually have a hydroxyl number of less than five. Below is an abstract of a procedure taken from ASTM Method D1957-61T for the determination of the hydroxyl number of fatty oils and acids.

**Reagents** *Neutral Pyridine*—Neutralize C. P. or reagent grade pyridine with 0.5 N alcoholic potassium hydroxide to a faint pink phenolphthalein end point.

*Pyridine Acetic Anhydride Reagent*—Dissolve 25% by volume of acetic anhydride in C. P. or reagent grade pyridine. This reagent should be freshly prepared before use.

*Neutral Butyl Alcohol*—Neutralize C. P. or reagent grade *n*-butyl alcohol with 0.5 N alcoholic potassium hydroxide to a faint pink phenolphthalein end point.

**Procedure** Determine the weight of sample to be used for the acetylation from Table 37.9.

TABLE 37.9 SAMPLE SIZE FOR HYDROXYL NUMBER DETERMINATION

Hydroxyl Number	Weight of Sample g
20	10
20 to 50	5
50 to 100	3
100 to 200	2

Weigh to the nearest 0.1 mg into a 250 ml Erlenmeyer flask with a ground glass joint the amount of sample specified in Table 37.9. Weigh 9.0 to 11.0 g of the sample into another flask for the acid value blank.

Pipet 5.0 ml of the pyridine acetic anhydride reagent into the flask containing the sample for acetylation. (For samples having a hydroxyl number between 0 and 20 add an additional 5 ml of neutral pyridine to the flask.) Pipet another 5.0 ml of the pyridine acetic anhydride reagent into an empty flask for the reagent blank. All 10 ml of neutral pyridine to the portion of the sample used for the acid number blank. Thoroughly mix the contents of each flask by gentle swirling. Insert reflux condensers into the Erlenmeyer flasks and heat on a steam bath for 1 hour. Add 10 ml of water through the condensers to the flasks and heat for an additional 10 minutes. Remove the flasks from the steam bath, mix the contents by swirling gently, and cool to room temperature.



Add 25 ml. of neutral butyl alcohol (about half through the condensers) to each flask so that it washes down the stoppers and sides of the flasks. Rotate so as to mix contents thoroughly. Add 5 drops phenolphthalein indicator to each flask, and titrate to a faint pink end point that persists upon replacing the stopper and shaking thoroughly.

Calculation.—Calculate the hydroxyl number as follows:

$$\text{Hydroxyl Number} = \frac{\left[ \left( A + \frac{BC}{D} \right) - E \right] F}{B},$$

where  $A$  = ml. of potassium hydroxide solution required for titration of the reagent blank,

$B$  = g. of sample used for the determination,

$C$  = ml. of potassium hydroxide soln. required for titration of the acid number blank,

$D$  = g. of sample used for the acid number blank,

$E$  = ml. of potassium hydroxide solution required for titration of the acetylated sample, and

$F$  = mg. of potassium hydroxide per ml. of standard potassium hydroxide solution.

#### POLYHYDRIC ALCOHOLS FRACTION

The aqueous phase remaining from the fatty acids separation contains the polyols. A.S.T.M. Method D1615-60 may be used for determining the amount of glycerol, ethylene glycol, and/or pentaerythritol in the aqueous phase. An abstract of this method is given below.

**Ethylene Glycol and Glycerol.**—The primary hydroxyl groups of ethylene glycol and glycerol are oxidized to formaldehyde by periodic acid; the secondary hydroxyl group of glycerol is oxidized to formic acid. By acidimetric and iodometric titration, the proportions of formic acid and formaldehyde respectively, can be determined, and calculated to glycerol and ethylene glycol.

**Procedure.**—Transfer the aqueous phase remaining from the fatty acids separation (page 1652) to a 400-ml. beaker and evaporate to about 60-ml. volume, using an electric hot plate as a source of heat. Keep the beaker covered with a watch glass during boiling.

Cool to room temperature, and filter through a rapid paper into a 100-ml. volumetric flask. Fill to the mark and agitate. The sample for the pentaerythritol determination as well as for the simultaneous determinations of glycerol and ethylene glycol will be taken from the flask.

Pipet 20 ml. ( $\frac{1}{3}$  aliquot) into a 1-liter Erlenmeyer, glass-stoppered flask (NOTE 1). Add 2 drops of methyl purple indicator (NOTE 2), and neutralize with 0.1  $N$  sodium hydroxide solution. Pipet into the 1-liter flask also 50 ml. of freshly prepared periodic acid solution (11 g. per liter), stopper, and swirl to mix thoroughly.

Simultaneously prepare two blanks containing 20 ml. of water. Allow to stand for 50 to 70 minutes at room temperature.

To the aliquot of the sample and the blank, add 100 ml. of water and 3 drops of methyl purple indicator and titrate with standardized 0.1  $N$  sodium hydroxide solution to neutrality. Use a 50-ml. buret and record the volume to the nearest 0.01 ml.

To the solution that has just been titrated add 150 ml of water, 30 ml of potassium iodide solution (200 g per liter) and 25 ml of sulfuric acid (1.2). Titrate with standardized 0.2 N sodium thiosulfate solution to a faint iodide color add 10 ml of starch indicator and titrate to the disappearance of the blue color.

NOTES—1 The aliquot should be so chosen if possible so that 15 to 20% of the periodic acid is consumed during the oxidation. Considerable excess of periodic acid is required to complete the oxidation and in case more than 20% is consumed the results should be disregarded and a smaller aliquot taken. On the other hand too small an aliquot is not advisable for the difference between titration and blank may be so small that any titration errors are magnified.

2 Methyl purple indicator manufactured by the Fleisher Chemical Co. Benjamin Franklin Station Washington 4 D C U S Patent No 2 416 619 has been found satisfactory.

Calculation—Calculate the percentage of glycerol  $G$  as follows

$$G = \frac{(A - B) \times N \times 0.09206 \times 100}{W \times F}$$

where  $A$  = ml of NaOH solution required for titration of the sample  
 $B$  = ml of NaOH solution required for titration of the blank,  
 $N$  = normality of the NaOH solution  
 0.09206 = grams of glycerol equivalent to 1 ml of 1 N NaOH solution,  
 $W$  = grams of sample used and  
 $F$  = aliquot fraction =  $\frac{1}{5}$

Calculate the percentage of glycerol and ethylene glycol  $T$ , as a percentage of glycerol as follows

$$T = \frac{(B' - A') \times N \times 0.023015 \times 100}{W \times F}$$

where  $A'$  = ml of  $\text{Na}_2\text{S}_2\text{O}_3$  solution required for titration of the sample,  
 $B'$  = ml of  $\text{Na}_2\text{S}_2\text{O}_3$  solution required for titration of the blank,  
 0.023015 = grams of glycerol equivalent to 1 ml of 1 N  $\text{Na}_2\text{S}_2\text{O}_3$  solution,  
 $N$  = normality of the  $\text{Na}_2\text{S}_2\text{O}_3$  solution,  
 $W$  = grams of sample used, and  
 $F$  = aliquot fraction =  $\frac{1}{5}$

If  $E$  is the percentage of ethylene glycol then  $E = 1.348(T - G)$

When  $E$  on the sample is free of ethylene glycol. In practice samples containing no ethylene glycol have given calculated  $E$  values of up to 1%. Therefore samples with  $E$  values of 1% or less should be considered as containing no ethylene glycol and samples with higher  $E$  values may be corrected 1% at the discretion of the analyst.

**Pentaerythritol**—Monopentaerythritol reacts with benzaldehyde to form a dibenzyl which is crystalline and can be handled gravimetrically.

**Procedure**—Transfer an aliquot of the sample solution from the 100 ml volumetric flask (see the procedure above) containing 0.15 to 0.55 g of pentaerythritol to a 100 ml beaker. Evaporate on a steam bath to a volume of about 5 ml. To the hot solution (incipient boiling) add 15 ml of benzaldehyde-methanol reagent (prepared by adding 100 ml of anhydrous methanol to 20 ml of benzaldehyde).

and 12 ml. of hydrochloric acid (sp. gr. 1.19). Swirl and allow to stand at room temperature for 15 minutes, swirling occasionally to prevent the precipitate from adhering to the bottom of the beaker. Place the beaker in an ice bath, maintaining the temperature at 0 to 2°C. for 1 hour or more.

Remove the reaction mixture from the ice bath and immediately filter with suction through a weighed fritted-glass crucible of medium porosity. Rinse the beaker with 25 ml. of cold (0 to 2°C.) methanol wash solution (prepared by mixing equal volumes of anhydrous methanol and water) and add to the crucible. Continue to transfer and wash the precipitate with 100 ml. of the methanol-water solution at 20 to 25°C. as follows: Disconnect the vacuum line, pour a 10-ml. portion of the wash solution from the beaker into the crucible, and stir the precipitate to form a homogeneous slurry, using a short flat-end glass rod. Connect the vacuum line and draw the wash solution through the crucible. Repeat this washing operation 6 times. With 30 ml. of the methanol-water wash solution, rinse the crucible walls, and rinse and remove the stirring rod.

Aspirate thoroughly and dry the precipitate at 105°C. for 2 hours, cool in a desiccator, and weigh.

Calculation.—Calculate the percentage of monopentaerythritol,  $P$ , as follows:

$$P = \frac{(W_2 + 0.0269) \times 0.436 \times 100}{W_1 \times F},$$

where  $W_1$  = grams of sample,

$W_2$  = grams of precipitate,

$F$  = aliquot fraction of sample,

0.436 = gravimetric factor for pentaerythritol, and

0.0269 = empirical correction for slightly soluble precipitate.

To convert the percentage of monopentaerythritol to the percentage of commercial technical monopentaerythritol divide  $P$  by 0.85. This conversion is based on the assumption that the commercial grade contains 85% monopentaerythritol.

*Separation of Less Common Polyhydric Alcohols.*—In many cases polyols other than glycerol, ethylene glycol, or pentaerythritol are present. When the identity of the polyol fraction is not known, isolation of the polyol or polyols may be helpful. Following is a procedure for separation of the polyol fraction which has been successful in the authors' laboratory.

*Procedure.*—Boil the aqueous phase remaining from the fatty acids separation (page 1652) for about 30 minutes to remove the ether present. Cool the solution and pass through both strong cation and strong anion exchange resins to remove all ions present (NOTE 1). Evaporate the deionized solution to approximately 50 ml. on a steam bath. Transfer the remaining solution to a tared 100-ml. beaker. Evaporate contents of the beaker to about 20 ml. on a steam bath. Continue evaporation of the solution at 60°C. until the solution becomes noticeably more viscous. Place beaker and contents in a desiccator overnight or longer to remove the remaining water.

The separated polyol may be identified by the usual qualitative chemical and physical tests. The polyol usually can be identified most rapidly by means of infrared spectroscopy. Infrared spectra of polyols usually found in alkyd resins may be found in reference <sup>52</sup> (NOTE 2).

<sup>52</sup> Shay, J. F., Silling, S., and Stafford, R. W., *Anal. Chem.* 26, 652, 1954.

NOTES—1 Dowex 50X8 in the hydrogen form has been found to be a satisfactory cation exchange resin. Dowex IX in the hydroxyl form has been found to be a satisfactory anion exchange resin.

2 The authors have found that the individual polyhydric alcohols may be separated from an aqueous solution containing 5% total polyhydric alcohols by weight. A 15 microliter sample of the solution is injected into a gas chromatograph equipped with a Carbowax 20M teflon column maintained at 220°C and a helium flow rate of 80 ml per minute.

### ACID NUMBER AND HYDROXYL NUMBER

The characteristics and performance of an alkyd resin are influenced appreciably by the amounts of free carboxylic acid groups and hydroxyl groups. Also the amounts of these groups must be known to establish the total composition of the resin. The acid number and the hydroxyl number are a measure of the free carboxylic acid and the free hydroxyl respectively. The procedures for determining both the acid number and the hydroxyl number of an alkyd are the same as the procedures given for the fatty acids fraction (page 1652).

### STYRENATED ALKYD RESINS

The composition of a styrenated alkyd resin may vary with the type of oil or fatty acid used, the amount of styrene and the process of manufacture. If a highly conjugated unsaturated fatty acid or oil is used, appreciable reaction with the styrene or polystyrene would be expected. If the oil or fatty acid contains little conjugated unsaturation, less copolymerization with the styrene or polystyrene would be expected. The difficult parts of the analysis of styrenated alkyd resins are the determinations of the amounts of fatty acids and polystyrene present, the degree of reaction between the polystyrene and the fatty acids, and the identity of the original oil or fatty acid. Any reaction between the oil or fatty acid and the styrene changes both the equivalent weight and the unsaturation of the fatty acid or oil. This, of course, changes all the physical and chemical characteristics by which the oil or fatty acid usually is identified. In analyses made of styrenated alkyd resins in the authors' laboratory, the fatty acid fraction always contains some polystyrene, and the polystyrene fraction always contains some fatty acids. It is not known definitely whether the polystyrene and fatty acids are chemically combined or whether complete physical separations were not obtained.

The dicarboxylic acids content of a styrenated alkyd resin may be determined by the methods given on page 1650.

One of the better methods evaluated in the authors' laboratory for the separation of the polystyrene is a method published by Swann.<sup>53</sup> Swann's procedure is given below.

**Procedure.**—Transfer the filtrate from the dicarboxylic acid determination (page 1650) to a 400 ml beaker. Evaporate the solvents under a hood by means of an 80°C glycol bath and a stream of air. When the solvent volume has been reduced to approximately 5 ml, add 5 ml of absolute methanol, agitate the sample and continue the evaporation to apparent dryness. If the sample contains appreciable styrene monomer, repeat the evaporations with methanol.

Mix 15 ml of water with 100 ml of absolute methanol and add to the residue. Cover the beaker, and heat the beaker and contents in a bath at 65°C. Stir the residue every 10 minutes with a glass stirring rod. Loosen portions of solid matter

<sup>53</sup> Swann, M. H., *Anal. Chem.* 25, 1735 (1953).

from the sides and bottom of the beaker. Break up lumps or large particles with the rod. After 30 minutes remove the beaker from the bath and allow its contents to cool. Remove the insoluble residue by filtration through a dried, tared fritted glass crucible of coarse porosity which previously has been prepared with a mat of asbestos. When all the methanol solution has drained through the crucible, continue the transfer of the residue with water. When all the residue has been transferred to the crucible, continue washing with water until the washings show no alkalinity when tested with indicator paper. Dry the residue at 110°C., cool, and weigh.

The residue generally consists almost entirely of polystyrene. A few carboxylate groups (potassium salts of fatty acids mixed or copolymerized with the polystyrene) will be present. The amount of these salts may be approximated by infrared or titrimetric methods.

NOTES.—1. Nearly all the fatty acid salts generally will be in the filtrate from the polystyrene determination. The fatty acids may be recovered by the procedure given on page 1652. The separated fatty acids generally will contain a small amount of copolymerized polystyrene. The amount of polystyrene may be estimated by determining the acid number of the separated fatty acids. Fatty acids generally used in the manufacture of styrenated alkyd resins have an acid number of about 200.

2. Except for rather volatile glycols, the use of which is rather doubtful in styrenated alkyd resins, the polyols will be present in the filtrate from the fatty acids determination. The polyols may be determined and identified by the methods given in the section on Alkyds (page 1655).

3. The acid number and hydroxyl number of the styrenated resin may be determined by the procedures given in the section on the Fatty Acids Fraction, above.

### CALCULATIONS

A generally accepted check on the accuracy of an analysis involves adding the weights of each constituent determined and seeing if the sum of the weights of the constituents equals the weight of the original sample. Because of the nature of the saponification reaction, the sum of the weights of the separated constituents of an alkyd resin is greater than the weight of the resin sample analyzed. The esterification reactions involved in the manufacture of the resin result in the formation and loss of water; conversion of the ester into its original constituents results in the consumption of the same amount of water. Consequently, to check the accuracy of a given alkyd analysis, the amount of resin corresponding to the amount of constituents found by analysis must be calculated and compared with the amount of resin sample taken for the analysis.

The calculation of the amount of resin corresponding to the amounts of constituents found is made on the basis of 100 g. or on a percentage basis. It involves calculating the "equivalents" of carboxylic acids and hydroxylic compounds (alcohols) used in making the alkyd and the amount of water lost in the esterification reactions. The equivalent weights given in Table 37-10 are used in these calculations. Calculation of the following quantities are made as part of the overall calculation: (a) equivalents of total acid, (b) equivalents of uncombined acid, (c) equivalents of combined or reacted acid, (d) water loss, (e) equivalents of total hydroxyl, (f) equivalents of uncombined hydroxyl, (g) equivalents of combined or reacted hydroxyl, (h) corrected polyhydric alcohol concentrations, (i) normalization of results, and (j) presentation of results. The calculation is illustrated with the example given below in which the analysis of the nonvolatile content (binder) of

TABLE 37-10 EQUIVALENT WEIGHTS OF ALKYD RESIN CONSTITUENTS

<i>Constituent</i>	<i>Equivalent Weight</i>
Phthalic Anhydride	74
Isophthalic Acid	84
Fumaric Acid	58
Maleic Anhydride	49
Azelaic Acid	94
Adipic Acid	73
Sebacic Acid	101
Glycerol	31.5
Pentaerythritol	34
Dipentaerythritol	43
Ethylene Glycol	31
Dipropylene Glycol	67
Propylene Glycol	32
Trimethylolethane	41
Coconut Fatty Acids	215
Linsced, Soya, or Dehydrated Castor Fatty Acids	282

an alkyd resin solution gave the following results when analyzed by the procedures given in the preceding sections

<i>Constituent</i>	<i>Result</i>	<i>Page Number of Procedure</i>
Phthalic Anhydride	32.5%	1650
Soya Fatty Acids	52.5	1651
Glycerol	4.7	1655
Ethylene Glycol	6.0	1655
Pentaerythritol	11.1	1656
<hr/>		
Total Uncombined	106.8%	
Acid Number	5.1	1653
Hydroxyl Number	45.7	1654

#### *A Equivalents of Total Acid.—*

The equivalents of phthalic anhydride in 100 g of binder

$$= \frac{\% \text{ Phthalic Anhydride}}{\text{Eq Wt of Phthalic Anhydride}} = \frac{32.5}{74} = 0.439$$

The equivalents of soya fatty acids in 100 g of binder

$$= \frac{\% \text{ Soya Fatty Acids}}{\text{Eq Wt Soya Fatty Acids}} = \frac{52.5}{282} = 0.186$$

Thus, the total acids equivalents in 100 g. of binder are the sum of the two numbers:  $0.439 + 0.186 = 0.625$ .

**B. Equivalents of Uncombined Acid.**—This number is obtained from the acid number which is defined as the number of milligrams of potassium hydroxide required to neutralize one gram of free acid. The acid number of the sample above is 5.1. Converting to the 100 g. basis and to equivalents from milliequivalents (i.e., milligrams),

$$\text{the equivalents of uncombined acids} = \frac{(\text{acid number})(100)}{(\text{Eq. Wt. KOH})(1000)} = \frac{(5.1)(100)}{(56.1)(1000)} = 0.009.$$

**C. Equivalents of Combined or Reacted Acid.**—This number is obtained by subtracting the equivalents of uncombined acid from the total acid:  $0.625 - 0.009 = 0.616$ .

**D. Water Loss.**—The equivalents of water formed (lost) during esterification are calculated from the acids rather than from the alcohols involved in the esterification because the acid concentrations found are regarded as more accurate. Thus, the equivalents of water which would be formed (lost) during the complete esterification of phthalic anhydride is  $0.439/2 = 0.220$  since only one equivalent of water is formed for each two equivalents of phthalic anhydride involved in the esterification. The equivalents of water which would be formed (lost) during the complete esterification of the soya fatty acids is  $0.186/1$  since one equivalent of water is formed per equivalent of fatty acids.

The total equivalents of water which would be formed (lost) during the complete esterification of all acid groups is the sum of the above two numbers:  $0.220 + 0.186 = 0.406$ . However, not all the acid groups were esterified during the manufacture of the alkyd resin analyzed because the resin has an acid number of 5.1. As shown above in B, an acid number of 5.1 corresponds to 0.009 equivalents of unesterified carboxylic acid per 100 g. of resin. Since one equivalent of water would be formed per free carboxyl group, the equivalents of water corresponding to the acid number are equal to the equivalents of free acid or 0.009. Thus, the water which was formed (and lost) during the manufacture of the resin is  $0.406 - 0.009 = 0.397$ .

The amount of water which would be lost in manufacturing 100 g. of the resin, i.e., the percentage water loss, is 0.397 multiplied by the equivalent weight of water or  $(0.397)(18) = 7.2\%$ .

**E. Total Hydroxyl Equivalents.**—

The total hydroxyl equivalents in 100 g. of binder, calculated from the polyhydric alcohol concentrations

$$= \frac{\% \text{ Glycerol}}{\text{Eq. Wt. Glycerol}} + \frac{\% \text{ Ethylene Glycol}}{\text{Eq. Wt. Ethylene Glycol}} + \frac{\% \text{ Pentaerythritol}}{\text{Eq. Wt. Pentaerythritol}} =$$

$$\frac{4.7}{31.5} + \frac{6.0}{31} + \frac{11.1}{34} = 0.669.$$

**F. Equivalents of Uncombined Hydroxyl.**—The hydroxyl groups represented in the hydroxyl number determination are not esterified. The equivalents of the unesterified or unreacted hydroxyl per 100 g. of binder as obtained from the hydroxyl number =  $\frac{(\text{hydroxyl number})(100)}{(\text{Eq. Wt. KOH})(1000)} = \frac{(45.7)(100)}{(56.1)(1000)} = 0.081$ .

**G Equivalents of Combined or Reacted Hydroxyl**—The total reacted equivalents of hydroxyl groups from the analyzed polyhydric alcohol determinations per 100 g of binder is  $0.669 - 0.081 = 0.588$

**H Corrected Polyhydric Alcohol Concentrations**—The combined ester equivalents based on the acid determinations are 0.616 while the equivalents based on polyhydric alcohols determination are 0.588. Obviously at least one of the results is inaccurate. Based on the authors experiences the acid determinations are more accurate than the polyhydric alcohol determinations. If the acid determinations are considered correct the amounts of the polyhydric alcohols should be adjusted accordingly. The adjustment may be made by multiplying the amount of each polyhydric alcohol by the sum of 0.616 (combined equivalents based on acid determinations) and 0.081 (uncombined equivalents based on hydroxyl number determination) and then dividing by 0.669 (total equivalents based on polyols determinations). Thus % Glycerol =  $(4.7)(0.697)/0.669 = 4.9\%$  % Ethylene Glycol  $(6.0) \times (0.697)/0.669 = 6.3\%$  % Pentaerythritol  $(11.1)(0.697)/0.669 = 11.6\%$

Based on these corrected values the total amount of the separated constituents is 107.8%. Conversion of the alkyd constituents to the alkyd resin would result in formation and loss of 7.2% water and the total recovered resin from the analysis then would be  $107.8 - 7.2$  or 100.6%. The experience of the authors has shown that a reliable analysis of an oil modified alkyd resin should result in a recovery within the range of from 98 to 101% and consequently the above recovery is considered satisfactory.

**I Normalization of Results**—If the recovery of the analysis falls within the limits given the analysis is considered accurate and reliable and the results may be normalized for comparison with other formulas. A summary of the actual corrected and normalized results are given below.

Constituent	% by Actual Analysis	% Corrected by Equivalent Calc	Normalized Percentages
Phthalic Anhydride	32.5%	32.5%	32.3%
Soya Fatty Acids	52.5	52.5	52.2
Glycerol	4.7	4.9	4.9
Ethylene Glycol	6.0	6.3	6.3
Pentaerythritol	11.1	11.6	11.5
	<hr/> 106.8%	<hr/> 107.8%	<hr/> 107.2%
Water Loss (calculated)	7.2	7.2	7.2
Total	<hr/> 99.6%	<hr/> 100.6%	<hr/> 100.0%

The normalized results in the right hand column were obtained by multiplying the results in the center column by the factor  $100.0/100.6$

**J Presentation of Results**—It is also convenient for comparative purposes to have the analysis reported in terms of the oil content on the normalized basis. The amount of oil corresponding to the fatty acids may be estimated by using an average equivalent weight for the polyols and calculating the amount of oil corresponding to the fatty acids. The calculations are shown below.



Average Equivalent Weight of Polyol =  $(31.5 + 31 + 34)/3 = 32.2$   
 Equivalent Weight of Fatty Acids = 282  
 Equivalent Weight of Oil =  $282 + 32.2 - 18 = 296.2$   
 $\%$  Oil (on normalized basis) =  $(52.2)(296.2)/282 = 54.8$

These results may be summarized and presented as follows:

<i>Uncombined</i>		<i>Combined</i>		<i>H<sub>2</sub>O Loss</i>
Phthalic Anhydride	32.3%	Phthalate Ester	45.2%	7.2%
Soya Fatty Acids	52.2	Soya Oil	54.8	
Glycerol	4.9			
Ethylene Glycol	6.3		100.0%	
Pentaerythritol	11.5			
	<hr/> 107.2%			

*K. Equivalent Weights.*—The equivalent weights of the constituents of alkyd resins will vary with purity and, in the case of fatty acids, with composition. Table 37-10 gives the approximate equivalent weights of some of the widely used constituents, and those used in the above calculation.

## BLEND OF ALKYD RESINS AND MELAMINE AND/OR UREA RESINS

### GENERAL

Urea-formaldehyde resins are condensation products of urea and formaldehyde. The resins suitable for protective and decorative coatings have been modified by etherification with an alcohol, usually butanol. Melamine-formaldehyde resins are very similar in composition to the urea-formaldehyde resins except that the urea is replaced with melamine. These resins are used extensively in combination with oil-modified alkyds in a variety of industrial baking enamels.

### INFRARED ANALYSIS

Miller and Shreve<sup>54</sup> have published a rapid infrared method for the quantitative estimation of both urea resins and melamine resins blended with alkyd resins. A thin film of resin solution is spread on a rock salt plate and dried for one hour at 60°C. in a vacuum oven. Absorbance values are measured at 5.8 microns for the alkyd resin, 6.1 microns for the urea resin, and 12.25 microns for the melamine resin.

### ANALYSIS BASED ON NITROGEN DETERMINATION

If only urea resin or melamine resin is mixed with an alkyd resin, the amount of amino resin may be estimated from the nitrogen content of the resin solution. A.S.T.M. Method D1013-52 may be used to determine the nitrogen content of the resin solution. The method is applicable for the determination of total nitrogen in resin solutions used in surface coatings. The method is not applicable for materials containing nitro groups. A summary of the method is given below.

*Procedure.*—Transfer a portion of the sample, weighed to the nearest 1 mg., to a Kjeldahl flask. The portion taken should contain from 150 to 250 mg. of nitrogen.

<sup>54</sup> Miller, C. D. and Shreve, O. D., *Anal. Chem.* 28, 200, 1956.

Add from 0.5 to 0.75 g of metallic mercury or the equivalent weight of mercuric oxide 10 g of potassium sulfate and 25 to 35 ml of sulfuric acid (sp gr 1.84). Mix the contents of the flask thoroughly place on the digestion rack, and heat slowly at first until the frothing subsides. Increase the heat until the acid boils briskly and continue the digestion for 2 hr after the solution becomes colorless or nearly so.

Allow the flask to cool add about 500 ml of water and a little granular zinc or a few pieces of inert irregularly shaped particles to prevent bumping. Add an excess (25 to 30 ml) of potassium sulfide sodium sulfide or sodium thiosulfate solution (40 g of  $K_2S$  or  $Na_2S$  or 80 g of  $Na_2S_2O_4 \cdot 5H_2O$  per liter). If  $Na_2S_2O_4$  solution is used it should be mixed with the NaOH solution (760 g per liter) so that both are added together. Add an excess (80 to 90 ml) of sodium hydroxide solution (760 g per liter) pouring it slowly down the side of the flask so that it doesn't mix at once with the acid solution. Immediately connect the flask to a connecting bulb (Davison type or bulb equally effective in preventing mechanical carry over) and condenser and mix the contents of the flask thoroughly.

Distill the solution into 50 ml of 0.5 N hydrochloric or sulfuric acid making certain that a connecting tube made of moderately heavy wall glass tubing 6 to 8 in in length leads from the condenser and extends below the surface of the acid in the receiver. Continue the distillation until the ammonia has been collected in the receiver (about 300 ml of distillate).

Add 5 to 7 drops of methyl red or methyl purple indicator and titrate the excess acid with 0.5 N standardized sodium hydroxide solution.

Make a blank determination following the same procedure and using the same amounts of all reagents.

Calculation—Calculate the percentage of nitrogen as follows

$$\% \text{ Nitrogen} = \frac{(A - B) \times N \times 0.014 \times 400}{W \times S}$$

where  $A$  = ml of NaOH solution required for titration of the blank,  
 $B$  = ml of NaOH solution required for titration of the sample,  
 $N$  = normality of the NaOH solution,  
 $W$  = grams of sample taken for the analysis, and  
 $S$  = fractional nonvolatile content of sample

The approximate amount of urea resin present may be calculated by multiplying the amount of nitrogen by 5.51. The approximate amount of melamine resin present may be calculated by multiplying the amount of nitrogen by 4.08.

If both melamine and urea resins are in the resin solution the amount of neither resin can be accurately determined from the nitrogen content. Swann and Esposito<sup>55</sup> have published a method by which the nitrogen of the urea resin only may be determined. The amounts of both urea and melamine resins may be calculated.

### ANALYSIS BASED ON SAPONIFICATION

The alkyd portion of an alkyd amino resin blend may be analyzed reasonably well by means of the methods given in the section for the analysis of alkyd resins. The dicarboxylic acids content may be determined according to the method given

<sup>55</sup> Swann M. H. and Esposito G. G. Anal. Chem. 28, 1984 (1956)

on page 1650. Although amino resins reportedly interfere with the determination the authors have found the interference to be almost negligible in most cases. Fatty acids separated by means of the method given on page 1652 may contain reaction products of the amino resins. Most of these products usually may be eliminated by adding about 10 ml. of ether to the fatty acid fraction and then centrifuging. Amino resins interfere with the method given for determining ethylene glycol, glycerol and pentaerythritol (Polyhydric Alcohols Fraction, page 1655). The gravimetric method outlined in this section, however, should be satisfactory in most cases for determining the polyols.

After the alkyd resin constituents have been determined quantitatively, the amount of alkyd resin may be calculated as in the section on Calculations, page 1659. (The acid number and hydroxyl number of the alkyd resin cannot be determined because the amino resins interfere. Consequently, the corrections usually made in alkyd resin calculations for the free carboxyl groups and free hydroxyl groups cannot be applied as indicated in the section on Calculations. However, these corrections are usually very small.) The amount of amino resins present should be the difference between the total resin content (i.e., the total nonvolatile vehicle content) and the alkyd resin content. In all quantitative determinations involving amino resins or blends of these resins with other resins, it must be remembered that amino resins do not have true nonvolatile contents. The resins continuously lose weight when they are heated. The nonvolatile content obtained varies with temperature, time of heating and thickness of film. Care must be taken that all comparisons be made as nearly as possible under identical test conditions. (See the section on Nonvolatile Content.)

#### DETERMINATION OF MELAMINE BY ACID HYDROLYSIS

A method for the determination of melamine-formaldehyde resin content of blends with alkyds and epoxy resins reported by Swann and Esposito has been found to be useful by the authors.<sup>56</sup> The method is based upon the insolubility of the acid hydrolysis products of melamine in dioxane, which is a good solvent for most coating resins. The procedure involves refluxing the resin blend containing the melamine resin in a hydrochloric acid-dioxane mixture, weighing the precipitate formed, and calculating the melamine content by experimentally established factors. An abstract of the procedure is given below.

**Procedure.**—Weigh a sample of the alkyd blend representing 0.125 to 0.300 g. of amino resin into a 250-ml. Erlenmeyer flask having a 24/40 ground-glass joint and dissolve in highest purity dioxane (NOTE 1). Add 1.50 ml. of 6 *N* hydrochloric acid with swirling of the sample.

Allow the sample to stand at room temperature for 30 minutes. Then attach an air condenser to the sample flask and place it in a water bath at 60°C. After 2 hours, cool to room temperature and filter through a weighed, fritted-glass crucible of medium porosity, transferring and washing the precipitate with from 75 to 100 ml. of dioxane. Draw air through the crucible for 5 minutes. Then place in a vacuum oven at 50°C. and dry to constant weight (about 2 hours), cool, and weigh. Calculate results (NOTE 2).

**Calculation.**—In cases where no urea is present the weight of the precipitate can be calculated to melamine by the factor 0.540, or to melamine-formaldehyde resin by the factor 1.610.

<sup>56</sup> Swann, M. H. and Esposito, G. G., *Anal. Chem.* 29, 1361, 1957.

In cases where urea is present (NOTE 2) the following formula must be used

$$\% \text{ Melamine} = \frac{[A - (B \times C \times 0.0161)] \times 0.54 \times 100}{B \times S}$$

where  $A$  = weight of precipitate

$B$  = weight of sample used in analysis

$C$  = per cent of urea, and

$S$  = fractional nonvolatile content of sample

NOTES—1 Dioxane from Fisher Scientific Company Catalog Item D 53 has been found to be satisfactory

2 When urea resin is present it must be determined by the saponification method of Swann and Esposito<sup>55</sup> and a correction must be made

## BINDERS CONTAINING ROSIN

### GENERAL

Rosin is composed mostly of abietic and related acids. Approximately 10% of neutral material is also present. Rosin may be reacted with inorganic materials to form various rosin salts such as calcium and zinc. Rosin esters of methanol, ethanol, glycerol, ethylene glycol, pentaerythritol, and other alcohols are manufactured. Rosin may be reacted with maleic anhydride or fumaric acid to form rosin adducts. The adducts may be esterified with monohydric or polyhydric alcohols. Rosin often is hydrogenated or reacted with phenol-formaldehyde condensation products. Other rosin products are also manufactured. These various rosin products may be found in paints, varnishes, or lacquers.

### DETERMINATION OF ROSIN

Due to the wide variety of rosin products used in so many types of paints, varnishes, and lacquers, standard methods for the determination of rosin with broad applicability have not been developed. Tentative ASTM Method D1469-58T is applicable to the determination of rosin in normal rosin esters, varnishes, and orthophthalate alkyd resins which have not been modified by such materials as maleic or fumaric acid or phenols. An abstract of the method is given below.

**Procedure**—Transfer to a 500 ml Erlenmeyer flask with a ground glass joint an amount of sample containing approximately  $40 \pm 2$  g of nonvolatile material. Weigh the sample to the nearest 0.1 g. Add 150 ml of ethylene glycol-potassium hydroxide solution (132 g of potassium hydroxide per liter of ethylene glycol) and swirl to disperse the sample. Add a boiling stone, attach an air condenser to the flask, and reflux on a hot plate for 2 hr.

At the end of the 2 hr refluxing period, remove the solution from the hot plate and cool to room temperature under tap water. Add 100 ml of water and while cooling under tap water, add 40 ml of concentrated hydrochloric acid (sp gr 1.19). Place on the hot plate again, reflux for 5 min, and cool under tap water.

Transfer the sample quantitatively to a 1 liter separatory funnel with the aid of a total of 150 ml of water followed by two 30 ml rinses of benzene. Mix, allow the layers to separate, and draw off the lower aqueous layer into a second 1 liter separatory funnel. Extract the aqueous layer with two successive 60 ml portions of benzene and drain the aqueous layer into a third 1 liter separatory funnel. Combine the benzene extracts and wash with three 30-ml portions of water.

Transfer the washed benzene extract to a 400 ml beaker with the aid of a total

of 25 ml. of benzene. Add a boiling stone, and evaporate the benzene on a steam bath.

With the aid of a total of 100 ml. of methanol, transfer the residue of a 500-ml. Erlenmeyer flask having a ground-glass joint, add a boiling stone, and swirl to dissolve the oil. Slowly add 5 ml. of sulfuric acid (sp. gr. 1.84) while cooling under tap water. Attach an air condenser to the flask, and reflux on a hot plate for 10 min. Cool to room temperature under tap water.

Add about 250 ml. of sodium sulfate solution (100 g. per liter) to a 1-liter separatory funnel. Pour the contents of the flask into the funnel, and complete the transfer with 100 ml. of benzene. Shake thoroughly, allow to settle, and draw off the salt layer. Wash the benzene layer again with two successive 250-ml. portions of the salt solution. The last wash should be neutral to methyl orange; if not, continue the washings with 50-ml. portions of sodium sulfate solution until neutrality is obtained.

After removing the last wash, draw off the benzene layer into a 400-ml. beaker, using a total of 75 ml. of ethanol to complete the quantitative transfer.

Complete the determination by the indicator method below, or by the potentiometric method following.

**Indicator Method.**—Add 1 ml. of thymol blue indicator and titrate with a standardized methanol solution of potassium hydroxide (0.2 *N*) to the appearance of a blue or blue-green color.

**Potentiometric Method.**—Titrate with a standardized methanol solution of potassium hydroxide (0.2 *N*) to an apparent pH of 10.5.

**Calculation.**—Calculate the percentage of rosin, expressed as abietic acid, as follows:

$$\text{Rosin Acids, \%} = \frac{A \times N \times 30.2}{W \times S},$$

where *A* = ml. of potassium hydroxide solution used for titration of sample,

*N* = normality of the potassium hydroxide solution,

*W* = grams of sample taken for analysis, and

*S* = fractional nonvolatile content of sample.

#### ROSIN IN ROSIN-CONTAINING BINDERS

The authors have found the methods given in the section for alkyds (page 1650), with a few modifications and additions, to be useful in the analysis of most rosin containing binders. The same saponification procedure may be used and all the fractions (dicarboxylic acids, if present, unsaponifiable, fatty acids, and polyols) may be separated in the usual manner. A larger sample than specified may be necessary to obtain larger fractions in order to make further analyses. Also, in case of cellulose nitrate lacquers, the cellulose nitrate must be removed by the procedure given for the analysis of cellulose nitrate (page 1670).

The dicarboxylic acid fraction (in case of blends with alkyd resins or lacquers containing esters of dicarboxylic acids as plasticizers) and the polyol fraction (from alkyd resin, oil, or rosin ester) should require no further treatment.

The unsaponifiable of alkyd resins or unmodified oils usually does not exceed one per cent of the total nonvolatile binder. The saponification procedure used in the analysis of alkyd resins, however, does not result in complete saponification of rosin esters. and some rosin ester is found in the unsaponifiable fraction. The

either heat-reactive (appreciable methylol groups present) or non-heat-reactive (little or no methylol groups present). Non-heat-reactive resins generally are produced with less formaldehyde and with acid catalysts.

Phenols used in the manufacture of phenolic resins include phenols, cresols, xylenols, 2,2-bis(*p*-hydroxyphenyl)propane commonly known as bisphenol-A, *p*-phenylphenol, *p*-*tert*-butylphenol, and *p*-*tert*-amylphenol. Resins produced with phenols having a substituent group in the *para* position have lighter color and better color stability. Resins produced with phenol, *m*-cresol, 3,5-xenol, and bisphenol-A are not oil soluble unless modified with rosin or rosin ester.

### PHENOLIC RESIN SOLUTIONS

Phenolic resins in solvent solutions usually can be identified rather completely by means of infrared spectroscopy. A film of the resin may be obtained by evaporating the resin solution under vacuum at 60°C. Higher temperatures should not be used because such resins are nearly always the heat-reactive type. Shreve<sup>57</sup> has pointed out the use of infrared spectroscopy in the identification of phenolic resins. Below are observations based on Shreve's work and the authors' experiences which should aid in identifying a phenolic resin by means of its infrared spectrum:

1. Phenolic and alcoholic hydroxyl groups absorb near 3 microns. A broad deep band in this region of the spectrum is indicative of a large amount of methylol groups, and therefore, of a heat-reactive resin. Methylol groups absorb near 9.4 microns. High absorbance in this region is indicative of a high methylol content, and hence, a heat-reactive group.

2. Alkyl groups absorb near 3.4 microns. Alkyl substitution in the phenol may be detected by a band at 3.4 microns. The intensity of the band will be related to the amount of aliphatic hydrocarbons present. The infrared absorption spectrum of *p*-*tert*-butylphenol-formaldehyde (presented as Spectrum 13 in the section on Infrared Spectra) illustrates this.

3. Most phenolic resins give rise to a rather sharp band at 6.2 microns. Xylenols and cresols have a doublet near 6.2 microns.

4. *Para*-substituted phenolic resins give rise to a band at 11.45 microns. Spectra 13 and 14 in the section on Infrared Spectra illustrate this.

5. *Para*-phenyl phenolic resin has bands at 13.2 microns and 14.4 microns. The spectrum of *p*-phenylphenol-formaldehyde (number 14) in the section on Infrared Spectra illustrates this.

Determination of the alcoholic and the phenolic hydroxyl contents of the dried resin (60°C. under vacuum) may aid appreciably in characterizing the resin. The total hydroxyl content may be determined by the method (page 1654) for determining the hydroxyl number of fatty acids separated from alkyd resins. Alcoholic hydroxyl may be determined by phthalation with phthalic anhydride in pyridine.<sup>58</sup> Phenolic hydroxyl may then be calculated by difference.

### OIL VARNISHES AND VEHICLES

If an appreciable amount of phenolic resin is present in an oil varnish or vehicle, an infrared spectrum of the nonvolatile portion may aid in the detection and identification of the phenolic resin. Bands in the spectrum due to the resin usually may be detected readily. Spectrum 12 in the section on Infrared Spectra

<sup>57</sup> Shreve, O. D., Anal. Chem. 24, 1692, 1952.

<sup>58</sup> Elving, P. J. and Warshowsky, B., Anal. Chem. 19, 1006, 1947.

is a spectrum of a phenolic oil varnish. Most oils used with phenolic resins (linseed, tung, etc.) have about the same molecular weight and ester content and consequently most of the oils have about the same absorptivity at 5.75 microns (ester carbonyl band). The amount of oil in a phenolic resin binder therefore may be estimated by comparing the absorbance of 5.75 microns of the binder with that of an oil only. The ratio of the absorbance of the binder to that of the oil should approximate the fraction of oil in the binder.

Approximate quantitative analysis may be made sometimes by the methods given for the saponification and separation of the unsaponifiable matter and fatty acids of alkyd resins (page 1649). The filtration step for removal of the dicarboxylic acid salts after saponification is not necessary; instead the saponification solution should be evaporated directly to 25 ml. The unsaponifiable and fatty acid fraction may then be separated according to the procedures given under Fatty Acids Fraction (page 1652). Some phenolic resins may be insoluble and removal by filtration may be necessary. The unsaponifiable fraction usually consists almost entirely of phenolic resin. The fatty acid fraction usually consists of a combination of fatty acids and phenolic resin. Portions of the fatty acids and phenolic resin which are chemically combined cannot of course be separated. The phenolic resin which is not chemically combined may be separated by the method given for the separation of rosin and fatty acids (page 1666).

## CELLULOSE NITRATE

### GENERAL

A number of cellulose derivatives are used in surface coatings. The ester and ether derivatives particularly cellulose nitrate, cellulose acetate, butyrate, and ethyl cellulose are used in lacquer formulations. Other derivatives such as methyl cellulose and hydroxyethylcellulose may be found in lacquers or latex finishes. The use of cellulosic polymers in lacquers is most important. Perhaps the greatest advantage of lacquers is their rapid drying rate. Films of cellulosic polymers are usually very strong and tough but are sometimes lacking in adhesion, flexibility, and/or gloss. Resins and plasticizers are generally added to lacquers to improve these properties. The resins and plasticizers are also added to improve the degree of film building by increasing the solids content of the lacquer at spraying viscosity.

Cellulose nitrate is by far the most widely used cellulosic polymer. Two of the largest uses of this polymer are in automotive and furniture finishes. However, it may be used to coat almost any article where rapid drying is an important factor. Lacquers based on cellulose nitrate almost always also contain monomeric plasticizers and resins in addition to the polymer. The most commonly encountered plasticizers are the phthalate and phosphate types. The most widely used resins include the rosin esters, non-oxidizing short oil, glyceryl phthalate, alkyd resins, and linear type polyesters. The thinner portion of a cellulose nitrate lacquer generally contains ester, ketone, or alcohol solvents or mixtures of these plus a diluent.

A coating may easily be identified as a cellulose nitrate lacquer by detection of the nitrate bands in the infrared absorption spectrum of a film of the clear coating (or vehicle of the coating) as indicated in the section on Identification of Polymers, Resins, and Oils. The presence of strong absorption bands at 6.1 and 7.9 microns plus broad absorption at 12.0 microns generally are sufficient for detection of

cellulose nitrate. A spectrum of cellulose nitrate (No. 22) and a plasticized cellulose nitrate lacquer (No. 23) are given in the section on Infrared Spectra. Common plasticizers are listed in Table 37-2 and spectra of these plasticizers are also given in the section on Infrared Spectra. An infrared method for the quantitative determination of cellulose nitrate in the presence of other cellulose and resins normally compounded with cellulose nitrate also is available.<sup>59</sup>

There is no standard method applicable to the analysis of cellulose nitrate lacquers in general. However, there are some generally accepted procedures applicable to some common lacquer compositions. Swann<sup>60</sup> has reported methods for the analysis of cellulose nitrate lacquers containing phthalate plasticizers and/or alkyd resins. In this scheme the thinner in the lacquer vehicle is removed by pouring the vehicle into boiling water. The binder is recovered from the water-binder mixture by filtration and the cellulose nitrate is separated from the plasticizer and resin portions of the binder by treating the binder with a benzene-ethanol solvent. The precipitated cellulose nitrate is separated, dried, and weighed. From a determination of the total phthalate content of the filtrate by an ultraviolet method, the plasticizer and alkyd resin portion is calculated. When both phthalate plasticizer and alkyd resin are present, the plasticizer is isolated on a separate portion of the vehicle by adsorptive filtration through charcoal. Hanson<sup>5</sup> has reported an interesting method for separating monomeric plasticizers, resins, and cellulose nitrate by first dispersing the total lacquer (including pigment and thinner) on salt and then selectively extracting the plasticizer, resin, and cellulose nitrate by a Soxhlet procedure. Hanson's method is discussed in the section on Identification of Plasticizers (page 1640). Shaefer and Becker<sup>61</sup> have presented very useful methods for the determination of cellulose nitrate in the presence of alkyd resins and for the separation of alkyds from cellulose nitrate. Their separation method is based on the conversion of cellulose nitrate to a water-soluble form by reduction with ferrous chloride followed by the extraction of the alkyd resin with methylene chloride.

From the methods described above it can be seen that no single analytical scheme can be used for the complete characterization of all cellulose nitrate lacquer compositions. However, the application of a few general methods usually will make possible a reasonably complete quantitative analysis. The general outline for an analysis given below consists of the determination of the nonvolatile vehicle content, separation of the cellulose nitrate portion of the lacquer from the plasticizer and resin portion, and characterization of each portion.

### NONVOLATILE CONTENT

It is relatively difficult to obtain an accurate determination of the nonvolatile content of cellulose nitrate lacquers because these compositions release thinner rather slowly on the one hand and because some of the plasticizers in use are relatively volatile. For these reasons a modification of method *B* of the Foil Method (page 1642) or a special dish method (page 1618) should be used. Swann<sup>62</sup> has suggested a sample size representing 0.5 g. of nonvolatile vehicle for both the foil and the dish methods. In the foil method oven-drying is omitted and instead

<sup>59</sup> Rosenberger, H. M. and Shoemaker, C. J., *Anal. Chem.* 31, 1315, 1959.

<sup>60</sup> Swann, M. H., Adams, M. L., and Esposito, G. G., *Anal. Chem.* 27, 1426, 1955. See also, reference 6, p. 329.

<sup>61</sup> Shaefer, W. E. and Becker, W. W., *Anal. Chem.* 25, 1226, 1953.

<sup>62</sup> Kappelmeier, C. P. A., *op. cit.*, p. 334; see also reference <sup>59</sup>.



Remove the thimble from the extraction apparatus, allow to drain and then dry in an oven at  $105^{\circ} \pm 2^{\circ}\text{C}$ . to a constant weight. Save and combine all filtrates if the plasticizer is to be analyzed.

Calculation.—

$$\% \text{ Cellulose Nitrate} = \frac{R \times 100}{W \times S},$$

where  $R$  = grams of material in the thimble after extraction

$W$  = grams of sample taken, and

$S$  = fractional nonvolatile content of sample.

NOTE.—The above methods for separating cellulose nitrate may be varied with respect to solvent used, size of sample, time of extraction, etc. In order to obtain clean and complete separation of cellulose nitrate, modifications of the methods may be necessary for some lacquers. Obviously, complete separation is necessary for accurate quantitative analysis. Completeness of separation may be checked by means of the infrared methods discussed above or by spot tests given in the section on Qualitative Spot Tests (page 1632).

#### ANALYSIS OF CELLULOSE NITRATE FRACTION

The nitrate nitrogen content of the separated cellulose nitrate may be determined by the nitrometer method according to A.S.T.M. Method D301-56 or by a modified Kjeldahl method. A method found to be useful by the authors is that of Shaefer and Becker.<sup>61</sup> In this method the sample is dissolved in hot acetic acid and boiled with a special iron(II) reagent. The iron(III) produced by the oxidizing action of the nitrate is then titrated with standard titanous chloride. The Shaefer and Becker method is especially useful when only the cellulose nitrate content of the lacquer vehicle is desired because the method may be applied directly to the vehicle without prior isolation of the cellulose nitrate. When applied to the total vehicle, the amount of cellulose nitrate present is calculated by assuming the cellulose nitrate contains 12% nitrogen.

#### ANALYSIS OF THE PLASTICIZER AND/OR RESIN FRACTION

The plasticizer and/or resin portion may be obtained by careful evaporation of the solvent phase resulting from the cellulose nitrate separation. Methods for the identification of the plasticizers are discussed in the section on Identification of Plasticizers (page 1640). Rosin esters may be detected by the Liebermann-Storch test (page 1638). Haslam, Soppet, and Willis<sup>34</sup> have published methods for the infrared and chemical examination of plasticizers obtained from poly(vinyl chloride) compositions. Many of the plasticizers discussed are also found in cellulose nitrate formulations.

In many cases the plasticizer and/or resin portion may be analyzed by the methods given for the analysis of alkyd resins (page 1649). The data obtained in the analysis may require considerable interpretation. A few examples of how the data may be interpreted follow: the presence of phthalate ester and absence of fatty acids indicate the absence of alkyd resin; if the amount of polyhydric alcohol found is equivalent to the combined dicarboxylic acids and fatty acids fractions, the absence of monomeric phthalate ester is indicated; if the amount of polyhydric alcohol found is less than equivalent to the combined dicarboxylic acids and fatty acids fractions, both alkyd resin and monomeric phthalate ester are indicated; the presence of fatty acids and absence of dicarboxylic acids indicates the presence of an oil. If the data obtained in the analysis are sufficient to identify the components

present the amounts present usually can be calculated. If rosin ester is present in the plasticizer and/or resin portion it may be determined by the methods given in the section on Binders Containing Rosin (page 1666).

## CELLULOSICS OTHER THAN CELLULOSE NITRATE

### GENERAL

As indicated in the above section, cellulosics other than the nitrate are used in lacquer formulations. Important cellulosics other than the nitrate include cellulose acetate, cellulose acetate butyrate, and ethyl cellulose. Cellulose acetate has high resistance to heat and ultraviolet radiation. However, it is not compatible with many resins and plasticizers and is not soluble in many organic solvents. For these reasons its use is limited to coatings which must have high heat and ultraviolet resistance.

Cellulose acetate butyrate has better compatibility and solubility properties and is more widely used in such formulations as metal finishes, airplane lacquers, strippable coatings, and in paper coatings. Although the compatibility and solubility of the acetate butyrate is better than that of the acetate, it is not as good as that of cellulose nitrate. Both the acetate and the acetate butyrate polymers have good heat and light resistance and both are much less flammable than the nitrate.

Ethyl cellulose, an ether of cellulose, is more resistant to alkali than the cellulose esters but less resistant to acids. The ether is more flexible at low temperatures than are the cellulose esters and more resistant to heat and light than is cellulose nitrate. Ethyl cellulose is compatible with many resins, plasticizers, and waxes and is soluble in many organic solvents. It is used in paper and textile coatings, strippable coatings, fabric coatings, furniture lacquers, and lacquers formulated for exterior exposure.

### ANALYSIS

The same general scheme of analysis given in the preceding section for the analysis of cellulose nitrate coatings may be used for the analysis of coatings containing cellulose acetate, cellulose acetate butyrate, or ethyl cellulose. Infrared spectra of these polymers do not have such strong, distinctive bands as cellulose nitrate, and identification of the polymers in coatings by means of infrared spectra is more difficult. However, the spectra are sufficiently distinctive so that identification of the separated polymers can be made. Spectrum 24 in the section on Infrared Spectra is a spectrum of cellulose acetate, Spectrum 25 is a spectrum of cellulose acetate butyrate. A spectrum of ethyl cellulose is given in reference <sup>11</sup>. The Soxhlet extraction method given above (page 1672), with *n*-hexane as the extraction solvent, instead of ether, usually is satisfactory for the isolation of the plasticizer from coatings containing cellulose acetate, cellulose acetate butyrate, or ethyl cellulose. Genung<sup>63</sup> has published methods by which the cellulosic polymers may be analyzed. The plasticizer fraction may be analyzed by the methods given on page 1673 and in the section on Identification of Plasticizers, page 1610.

<sup>63</sup> Genung, L. B., *Anal. Chem.* **22**, 401, 1950.

## VINYL RESINS

## GENERAL

Vinyl polymers and copolymers, such as poly(vinyl chloride), poly(vinyl acetate), poly(vinyl chloride-acetate), poly(vinyl butyral), and poly(vinyl alcohol), are used in coatings formulations. The most widely used of these vinyls in lacquer formulations are the poly(vinyl chloride-acetate) copolymers, and consequently, these copolymers will be discussed further. The poly(vinyl chloride-acetate) copolymers have very high resistance to most chemicals. They are sufficiently soluble in solvent mixtures containing ketones to make application practical, and yet the applied film is unaffected by many solvents. The resins are colorless, odorless, tasteless, and non-toxic. Films of these resins are tough and have good abrasion resistance. Light and heat resistance and adhesion of the films are relatively poor, however. Poly(vinyl chloride-acetate) resins are used in coatings for metal containers, paper and fiber food containers, swimming pools and other masonry, and tanks.

Several varieties of poly(vinyl chloride-acetate) resins are manufactured. For maximum chemical and solvent resistance, resins with a high vinyl chloride content, approximately 95%, are produced. Resins with better solubility and compatibility contain about 87% vinyl chloride and 13% vinyl acetate. Hydroxyl groups are sometimes incorporated in the resins to improve compatibility. Some resins are modified with about 1% of a dicarboxylic acid, such as maleic acid, to improve adhesion.

Practically all lacquers based on poly(vinyl chloride-acetate) resins require plasticizers. Both monomeric plasticizers (such as dioctyl phthalate, tricresyl phosphate, and dioctyl sebacate) and polymeric or resinous plasticizers are utilized. Many resins, such as rosin esters, phenolic resins, and urea-resins are used with poly(vinyl chloride-acetate) resins containing hydroxyl groups.

## ANALYSIS

The presence of a poly(vinyl chloride-acetate) resin in a lacquer vehicle can be detected from the infrared spectrum of the nonvolatile portion of the vehicle by using the scheme given in Table 37-1. The infrared spectra of some vinyls are given in the section on Infrared Spectra: poly(vinyl chloride), No. 26; poly(vinyl acetate), No. 39; poly(vinyl chloride-acetate), No. 28; and a phthalate plasticized poly(vinyl chloride), No. 27. The spectrum of poly(vinyl chloride) has an absorption band at 7.5 microns and a broad band at about 14.5 microns both of which are not present in the infrared spectrum of poly(vinyl acetate). The spectrum of poly(vinyl acetate) contains a strong absorption band at 5.8 microns due to an ester carbonyl group. Both resins give rise to absorption at 7.0 microns, the absorption of the acetate being weak compared with that of the chloride. The spectrum of poly(vinyl chloride-acetate) is a composite of the spectra of poly(vinyl chloride) and poly(vinyl acetate), the intensity of the various absorption bands varying with the concentration of vinyl chloride and vinyl acetate in the copolymer. The spectrum of a vinyl terpolymer, poly(vinyl chloride-acetate-maleic acid), also is included in the section on Infrared Spectra to show that terpolymers containing only 1% maleic acid cannot be distinguished by the copolymer by means of their infrared spectra.

years but were used only in small-volume speciality uses until recently because of cost. The availability of lower cost monomers has made possible competitive use of the resins in many coatings. This in turn has resulted in development of many new types of polymers with better performance characteristics in paints and lacquers. Acrylic solution polymers are used in aircraft lacquers, automotive finishes, aluminum coatings, hardware lacquers, and other finishes. Development of emulsion polymers has resulted in appreciable usage of the resins in both interior and exterior latex house paints. The high ultraviolet light resistance of the acrylic resins makes the emulsion polymers particularly useful for exterior latex house paint where they are now being used widely. Until recently both solution and emulsion polymers have been thermoplastic and permanently soluble and fusible. However, at present both solution and emulsion polymers are available in which crosslinking agents are blended or copolymerized. These resins are thermosetting and become insoluble upon conversion by heat, are harder, and have better chemical resistance. These resins are used in appliance finishes.

### ANALYSIS

There are no standard methods for the analysis of acrylate coatings. However, there are some generally recognized methods for the analysis of methacrylate lacquer formulations. The polymer may be identified by means of the infrared spectrum of the nonvolatile vehicle portion of the lacquer via the scheme given in Table 37-1. The bands at about 8 microns have been used by the authors to distinguish a coating which is primarily a methacrylate from one which is primarily an acrylate. The methacrylates exhibit more or less of a doublet at 7.9 and 8.05 microns, whereas the acrylate exhibits a relatively broad, single absorption band at 8.0 microns. Spectra 30 and 32 in the section on Infrared Spectra are spectra of methacrylates; spectrum 31 is that of a phthalate plasticized methacrylate formulation.

As in the case with most lacquers, the binder portion of most methacrylate lacquers contain plasticizers in addition to the methacrylate homo- or copolymer. Consequently, the first step in the analysis of this type of coating involves the separation of the plasticizer and polymer portions of the binder. This may be done by the Soxhlet or solvent-nonsolvent method (page 1672). In the solvent-nonsolvent method acetone may be used as the solvent and petroleum ether may be used as the nonsolvent.<sup>64</sup> Swann and Esposito<sup>65</sup> have developed a saponification method for separating methacrylate polymers from plasticizers and other polymers. In this method the lacquer samples are diluted with acetone, air-dried to remove all thinner, dissolved in methyl ethyl ketone, saponified with alcoholic alkali, and poured into a large volume of dilute acid. The insoluble methacrylate polymer is then isolated by filtration. The method has been used to separate the methacrylate polymer from lacquers containing cellulose nitrate and plasticizers, such as dibutyl phthalate, tricresyl phosphate, and butyl benzyl phthalate.

The isolated polymer portion of the lacquer binder often can be identified from its infrared spectrum. However, a more sensitive way to determine the composition of copolymers is through a vacuum depolymerization technique followed by identification of the depolymerization products by gas chromatography, infrared

<sup>64</sup> Kappelmeier, C. P. A., *op. cit.*, p. 356.

<sup>65</sup> Swann, M. H. and Esposito, G. G., *Offic. Dig. Federation Soc. Paint Technology* 33, 63, 1961.

Many epoxy resin vehicles are solutions of epoxy resins only, to which curing catalysts are added before application. The epoxy resin may be detected by means of the tests discussed in the above paragraph. The amount of resin in such a solution may be obtained by means of a nonvolatile determination. Classification of the resin may be made by means of the melting point and epoxide content of the resin since the manufacturers of epoxy resins usually specify the limits for melting point and epoxide content of each resin supplied. In addition to the infrared method, A.S.T.M. Method D1652-59T may be used for determining the epoxide content. An abstract of this method is given below.

**Apparatus.** Buret, closed-reservoir type, the buret tip should be fitted with a rubber stopper of the proper size to fit the neck of the Erlenmeyer flask and the stopper should have an additional small hole to permit the escape of replaced air during titration.

Erlenmeyer Flasks, 50-ml. and 100-ml. capacity.

Magnetic Stirrer, adjustable speed.

Magnetic Stirring Bars, tetrafluoroethylene (Teflon) covered.

**Reagents.** Chlorobenzene.

Chloroform-Chlorobenzene Mixture (1:1).

Crystal Violet Indicator Solution.—Prepare a 0.1% solution of crystal violet in glacial acetic acid.

Glacial Acetic Acid.

Hydrogen Bromide, anhydrous.

Hydrogen Bromide in Acetic Acid, Standard (0.1 N).—See NOTES 1 and 2. Prepare by bubbling anhydrous HBr at a slow rate through glacial acetic acid until the desired normality is attained (approximately 8 g. of HBr per liter). Standardize daily against 0.1 g. of sodium carbonate accurately weighed and dissolved in 10 ml. of glacial acetic acid.

NOTES.—1. Reagent of 0.1 N concentration has been specified because as solutions exceed this concentration, they become progressively less stable.

2. Hydrobromic acid, 30 to 32% concentration in acetic acid, available from the Eastman Co. (Catalog No. 1161), has been found satisfactory for the preparation of 0.1 N HBr solution.

**Procedure.**—Weigh to the nearest mg. a quantity of sample that contains 0.001 to 0.002 gram equivalents of epoxy groups into an Erlenmeyer flask. Use a 50-ml. flask for low-molecular-weight resins (liquid grades) and a 125-ml. flask for high-molecular-weight resins (solid grades).

Dissolve the sample in a solvent at room temperature. Use 10 ml. of chlorobenzene for liquid grade resins and 25 ml. of a 1:1 mixture of chloroform and chlorobenzene for solid grade resins. Place a Teflon-sealed magnetic stirring bar into the flask and allow mixture to swirl on magnetic stirrer to effect solution.

Add 4 to 6 drops of crystal violet indicator solution and attach the flask to the rubber stopper on the buret tip. Lower the buret tip to a point just above the solution and titrate with the hydrogen bromide in acetic acid to a blue-green end point with the magnetic stirrer rotating at a moderate speed to avoid splashing. Slow down the titration near the end point to allow ample time for the reaction to take place. Titrate to as nearly as possible the same color at the end point as that obtained during standardization of the reagent.

Make a blank determination on the reagents in an identical manner.

**Calculations.**—Calculate the normality of the HBr in acetic acid as follows:

$$N = \frac{A \times 200 \times 5}{53 \times B},$$

where  $N$  = normality of the HBr in acetic acid,

$A$  = grams of  $\text{Na}_2\text{CO}_3$  used, and

$B$  = milliliters of HBr used

Calculate the epoxy content in gram equivalents of epoxy groups per 100 g of resin as follows

$$\text{Epoxy Content} = \frac{N \times (A - B)}{10 \times C},$$

where  $N$  = normality of the HBr in acetic acid

$A$  = milliliters of HBr used for titration of the sample,

$B$  = milliliters of HBr used for titration of the blank, and

$C$  = grams of sample used

Epoxy resins are widely used as esters of fatty acids or rosin. A colorimetric method for the determination of bisphenol type epoxy resins in esters as well as in their unmodified form and in silicone blends has been published.<sup>70</sup> Peacock and Pross have published an infrared method based on the absorption of the ester carbonyl group to determine the equivalent percentage of oil in such esters. Fatty acids may be separated and identified by means of the procedures given in the section for the analysis of alkyd resins. The ester may be saponified according to the procedure given in ASTM Method D563-52. If the resin precipitates during saponification, it should be removed by filtration. The fatty acids may be separated from the filtrate by means of ASTM Method D563-52.

Analysis of blends of epoxy resins with urea resins, melamine resins, or phenolic resins is rather difficult. The amount of urea resin or melamine resin may be estimated by means of the procedure given on page 1663 for the determination of urea or melamine resins blended with alkyd resin. In many cases the epoxy resin may be separated reasonably well from the other resins by the use of solvents. Most urea and melamine resins are soluble in alcohols. Most phenolic resins are soluble in alcohols or aromatic solvents. Most of the epoxy resins are almost completely insoluble in alcohols and aromatic solvents.

## IDENTIFICATION AND ANALYSIS OF PIGMENTS

### GENERAL

The pigment identification and analysis is performed on the pigment separated by the procedures given in the section on solvent type coatings (page 1621) or in the section on water type coatings (page 1626). While the number of pigments commonly used in paint is large, it is unlikely that more than a few pigments will be present in any one paint and in many cases only a single pigment will be present. In addition, it is usually not necessary to determine the small amounts of pigments used for tinting.

<sup>70</sup> Swann, M. H. and Esposito, G. G. *Anal. Chem.* **28**, 1006 (1956).

<sup>71</sup> Peacock, N. M. and Pross, A. W. *Offic. Dig. Federation Soc. Paint Technology* **27**, 702, 1955.

As indicated in the introduction to this chapter, the primary purpose of the pigment is to provide hiding power and color. In addition, the pigment affects various other properties, such as gloss and viscosity. The gloss of a coating may vary from the high gloss of a baking enamel through an intermediate satin or eggshell gloss to a complete flat finish. For the most part the gloss of a coating is controlled by the amount and type of pigment incorporated in the formulation. After sufficient hiding pigments have been added to obtain the hiding power desired, a lowering of gloss is obtained by the addition of non-hiding or extender pigments. For example, the high gloss of an enamel is due to the fact that it contains a much lower pigment content than a product referred to as a paint; and because of the necessary low pigment content, an enamel usually contains only hiding pigments.

The type and amount of pigment in a coating also determines to a great extent the consistency or viscosity of the final product. Pigments differ in their ability to adsorb oil or other binder materials. Thus the viscosity of the vehicle portion being constant, the viscosity of the finished material is determined by the amount and kind of pigments used. Control of the viscosity is particularly necessary to ensure proper application of the coating, whether by brushing, spraying, roller coating, or some other method.

The pigments as well as the binder make an important contribution to the dura-

TABLE 37-11. WHITE PIGMENTS COMMONLY USED IN PAINT

<i>Titanium Pigments</i>	<i>Chemical Constituents</i>
1. Titanium Dioxide	94-98% $\text{TiO}_2$ plus minor amounts of $\text{ZnO}$ , $\text{Al}_2\text{O}_3$ , $\text{Sb}_2\text{O}_3$ , and $\text{SiO}_2$ .
2. Titanium-Calcium	30% $\text{TiO}_2$ & 70% $\text{CaSO}_4$ or 50% $\text{TiO}_2$ & 50% $\text{CaSO}_4$ .
<i>Zinc Pigments</i>	
3. Zinc Oxide	98-99% $\text{ZnO}$ .
4. Lithopone	28% $\text{ZnS}$ plus $\text{BaSO}_4$ .
5. Leaded Zinc Oxide	50-88% $\text{ZnO}$ plus $\text{PbSO}_4$ . $\text{PbO}$ .
<i>Lead Pigments</i>	
6. Basic Silicate White Lead	47.9% $\text{PbO}$ , 47.9% $\text{SiO}_2$ , 4.2% $\text{SO}_3$ .
7. Basic Carbonate White Lead	62-75% $\text{PbCO}_3$ plus $\text{Pb(OH)}_2$ .
8. Basic Sulfate White Lead	$2\text{PbSO}_4$ . $\text{PbO}$ .
<i>Antimony Pigments</i>	
9. Antimony Oxide	Over 99% $\text{Sb}_2\text{O}_3$ .
<i>Extender Pigments</i>	
10. Talc	Natural Hydrated Magnesium Silicate.
11. Clays	Natural Hydrated Aluminum Silicate.
12. Mica	Natural Alkali Aluminum Silicate.
13. Whiting	98% $\text{CaCO}_3$ .
14. Barytes	98% $\text{BaSO}_4$ .
15. Quartz Silica	98% $\text{SiO}_2$ .
16. Diatomaceous Silica	87-95% $\text{SiO}_2$ .
17. Gypsum	Hydrated Calcium Sulfate.

TABLE 37 12 COLORED PIGMENTS COMMONLY USED IN PAINT

<i>Blue Pigments</i>	<i>Chemical Constituents</i>
18 Iron Blue	Ammonium Ferric Ferrocyanide
19 Phthalocyanine Blue	Copper Phthalocyanine Chelate
20 Ultramarine Blue	Complex Combination of Soda, Alumina, Silica, and Sulfur
<i>Yellow Pigments</i>	
21 Chrome Yellow	$\text{PbCrO}_4$ or mixture $\text{PbCrO}_4$ $\text{PbSO}_4$
22 Zinc Yellow	$\text{ZnCrO}_4$ containing about 41% $\text{CrO}_3$ & 40% $\text{ZnO}$
23 Cadmium Lithopone	$\text{CdS}$ & $\text{BaSO}_4$
24 Pure Yellow Iron Oxide	98-99% $\text{Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}$
25 Raw Sienna	Natural Hydrated Yellow Iron Oxide (35-72% $\text{Fe}_2\text{O}_3$ )
26 Yellow Ochre	Natural Clays Impregnated With Yellow Hydrated Iron Oxide (5-55% $\text{Fe}_2\text{O}_3$ )
27 Hansa Yellow 10G	Diazotized <i>p</i> -chloro <i>o</i> nitroaniline coupled with <i>o</i> -chloroacetoacetanilide
<i>Green Pigments</i>	
28 Chrome Green	Combination of Chrome Yellow & Iron Blue
29 Phthalocyanine Green	Chlorinated Copper Phthalocyanine Chelate
30 Chromium Oxide	99% $\text{Cr}_2\text{O}_3$
<i>Orange Pigments</i>	
31 Molybdate Orange	$\text{PbCrO}_4$ , Lead Molybdate, & $\text{PbSO}_4$
32 Chrome Orange	Basic Lead Chromate
33 Dinitraniline Orange	Diazotized 2,4 dinitroaniline coupled with 2-naphthol
<i>Brown Pigments</i>	
34 Pure Brown Iron Oxide	Blend of Pure Red, Yellow & Black Iron Oxides (92-98% $\text{Fe}_2\text{O}_3$ )
35 Metallic Brown	Natural Iron Ores Usually of Limonite or Siderite Type (48-88% $\text{Fe}_2\text{O}_3$ )
36 Raw Umber	Natural Hydrated Yellow Iron Oxide (40-55% $\text{Fe}_2\text{O}_3$ , 13-16% $\text{MnO}_2$ and Clay Minerals)
37 Burnt Umber	Calcined Raw Umber (44-55% $\text{Fe}_2\text{O}_3$ & 10-16% $\text{MnO}_2$ )
38 Burnt Sienna	Calcined Raw Sienna (50-73% $\text{Fe}_2\text{O}_3$ )
<i>Red Pigments</i>	
39 Pure Red Iron Oxide	98% $\text{Fe}_2\text{O}_3$
40 Red Iron Oxide	Natural Oxides or Mixtures of Natural and Synthetic Oxides (60-94% $\text{Fe}_2\text{O}_3$ )
41 Venetian Red	40% $\text{Fe}_2\text{O}_3$ , 60% $\text{CaSO}_4$
42 Cadmium Lithopone, Red	$\text{CdS}$ , $\text{CdSe}$ , & $\text{BaSO}_4$
43 Lithol Red, Barium	Diazotized 2-naphthylamine-1 sulfonic acid coupled with 2 naphthol, barium salt
44 Lithol Red, Calcium	Same As Above But Calcium Salt



TABLE 37-12. (Continued)

<i>Red Pigments</i>	<i>Chemical Constituents</i>
45. Para Red	Diazotized <i>p</i> -nitroaniline coupled with 2-naphthol.
46. <i>Ortho</i> -Chlorinated Para Red	Diazotized <i>o</i> -chloro- <i>p</i> -nitroaniline coupled with 2-naphthol.
47. Parachlor Red	Diazotized <i>o</i> -nitro- <i>p</i> -chloroaniline coupled with 2-naphthol.
48. Toluidine Red	Diazotized <i>m</i> -nitro- <i>p</i> -toluidine coupled with 2-naphthol.
49. Lithol Rubine	Diazotized 4-aminotoluene-3-sulfonic acid coupled with 2-hydroxy-3-naphthoic acid, calcium salt.
50. BON Manganese Red	Manganese salts of various amines coupled with 2-hydroxy-3-naphthoic acid.
51. Alizarine Red Lake	Alizarine Dye Precipitated On Inert Aluminum Hydrate, Calcium Phosphate-Sulfate Base.
<i>Maroon Pigments</i>	
52. Toluidine Maroon	Diazotized <i>m</i> -nitro- <i>p</i> -toluidine coupled with <i>m</i> -nitroanilide of 2-hydroxy-3-naphthoic acid.
<i>Black Pigments</i>	
53. Carbon Black	80-95% Fixed Carbon, 6-19% Volatile.
54. Lampblack	80-95% Fixed Carbon; Plus Complex Hydrocarbon Oils.
55. Bone Black	10-20% Carbon; 80-90% $\text{Ca}_3(\text{PO}_4)_2$ .
56. Black Iron Oxide	94-95% $\text{Fe}_3\text{O}_4$ .
<i>Other Pigments</i>	
57. Red Lead	95-98% $\text{Pb}_3\text{O}_4$ .
58. Graphite	40-80% Carbon Plus Mineral Ash.
59. Aluminum	Technical Grade Aluminum.
60. Zinc	Technical Grade Zinc.

bility of the coating, including its resistance to moisture, the ultraviolet rays of the sun, and various chemicals to which the film may be exposed. The pigments in a particular coating are those which have been found suitable for the conditions to which they will be exposed, whether for interior or exterior use.

Pigments may also be used to enhance greatly the corrosion resistant properties of a protective coating. In anti-fouling paints, the pigment is chosen for the fungicidal properties it may possess.

In Tables 37-11 and 37-12 are given lists of 60 of the pigments most commonly used in surface coatings. In this list the pigments are listed according to color. While the list is not complete, it includes the pigments encountered in the vast majority of practical cases. A more complete list of pigments available to the paint formulator can be found in the Raw Material Index.<sup>72</sup> In addition to classifying the pigments according to color, it is generally advisable to distinguish between inorganic and organic pigments. Accordingly, qualitative tests for the pigments

<sup>72</sup> National Paint, Varnish, and Lacquer Association, Raw Materials Index, National Paint, Varnish, and Lacquer Assoc., Inc., Washington 5, D. C., Sept. 1955.

in each of these broad classifications are given. In the inorganic field the analyst can proceed further and make quantitative determinations of some of the various metals and inorganic radicals present in the pigment or pigment mixture. From these determinations and a knowledge of the composition of the various pigments as shown in Tables 37 11 and 37 12 it is possible to estimate the amounts present. For the organic pigments it is generally sufficient to identify the pigment present. In many cases only one organic pigment will be present and in most of the other cases it will be present in small amounts as a tinting material. In the few cases where the organic pigment is present in a substantial amount in admixture with inorganic pigments the organic pigment may be separated by extraction with an organic solvent such as chloroform, dioxane or alcohol.

## TESTS FOR PRESENCE OF ORGANIC PIGMENTS

### GENERAL

All of the pigments in Tables 37 11 and 37 12 are classified as inorganic except numbers 19, 27, 29, 33, 43, 44, 45, 46, 47, 48, 49, 50, 51 and 52. For convenience carbon black, lampblack and bone black are classified as inorganic.

Organic pigments may be either pigment dyestuffs or precipitated colors. A pigment dyestuff is an organic compound which is practically insoluble in water so that no metallic group is necessary for its precipitation. Hansa Yellow, Para Red and Toluidine Red are examples of pigment dyestuffs. A precipitated color is prepared from an organic dye which is normally soluble in water but which is precipitated by the preparation of a metallic salt of the soluble compound. Lithol Red and Lithol Rubine are examples of precipitated colors.

### TESTS FOR ORGANIC PIGMENTS

Tests for detecting organic pigments are based upon either extraction or ignition of the pigment mixture. The first indication of the presence of an organic pigment in the analysis of the total paint may be observed in the supernatant washes obtained when separating the pigment by the extraction procedure given in the section on the Isolation and Determination of the Pigment (page 1621). At least a small part of the organic coloring matter usually dissolves in the extraction mixture imparting to it a rather clean, bright color. An extraction procedure for detecting organic coloring matter is given as part of ASTM Method D5050. This procedure was given for organic coloring matter in yellow, orange, red and brown pigments containing iron and manganese but it also can be used for other classes of inorganic pigments. An abstract of the ASTM extraction method and an ignition procedure found useful by the authors are given below.

**Extraction Procedure**—Boil 2 g. of the pigment sample with 25 ml. of water, let settle and decant the supernatant liquid. Boil the residue with 25 ml. of ethyl alcohol (95%) and decant as before. Boil the residue with 25 ml. of 1 N alcoholic sodium hydroxide solution and again decant. Boil another 2 g. portion of the sample with 25 ml. of chloroform, let settle and decant the supernatant liquid.

If any one of the above solutions is colored, organic coloring matter is indicated.

**Ignition Procedure**—Place a sample of the pigment in a porcelain crucible and ignite at a temperature of 600–700°C.

Organic colors will burn and in the case of pigment dyestuffs leave little or no ash. When the organic pigment is a precipitated color, an ash will remain.

## IDENTIFICATION OF INORGANIC PIGMENTS

### *QUALITATIVE CHEMICAL TESTS*

C. P. A. Kappelmeier has devised an excellent scheme for the identification of inorganic pigments present in mixtures.<sup>73</sup> This scheme is based on five simple preliminary tests, a main analysis of the components soluble and insoluble in acids, and a number of additional special reactions. The preliminary tests are particularly useful and are based on characteristic reactions of the components of the pigment portion with the following reagents: (A) 4 M hydrochloric acid, (B) 2 M acetic acid, (C) 4 M sodium hydroxide solution, (D) 1 M sodium carbonate solution, and (E) a mixture of about equal parts of ammonia (25 to 28%) and 2 M ammonium carbonate. To perform the tests about 0.3 to 0.5 g. of the pigment is treated in a test tube with 8 to 10 ml. of the solution in question.

Table 37-13 contains a summary of the observations made by Kappelmeier when the pigment is treated with the above reagents.

### *ELEMENTAL TESTS*

The tests given in the above section usually are sufficient for an identification of an inorganic pigment. When considered necessary, classical wet chemical methods for the detection of the elements may be applied to pigments.<sup>73</sup> In the authors' laboratory, x-ray fluorescence spectrography and flame photometry are used to detect, and in some cases, determine the inorganic elements found in paint.<sup>74</sup>

### *SPECTROSCOPIC AND DIFFRACTION METHODS*

As indicated above, x-ray fluorescence spectrography, flame photometry as well as optical emission spectrography may be used to detect the elements normally encountered in pigments. Infrared spectrophotometry and x-ray diffractometry are also powerful tools for identifying pigments, both inorganic and organic. Probably the most efficient way to identify any completely unknown inorganic material is first by emission spectrography (x-ray or optical), then by infrared, and finally by x-ray diffractometry. The elements are determined by emission, the polyatomic ions by infrared, and the combinations of the ions (the specific salts) by x-ray diffractometry.<sup>75</sup> Examples of the use of spectroscopic methods for pigment and paint analysis may be found in reference <sup>76</sup>. The infrared spectra of 30 inorganic pigments may be found in reference <sup>14</sup>; spectra of pigments may also be found in the Encyclopedia of Spectroscopy.<sup>15</sup>

<sup>73</sup> Kappelmeier, C. P. A., op. cit., p. 189.

<sup>74</sup> Snell, F. D., and Biffin, F. M., Commercial Methods of Analysis, McGraw-Hill Book Co., New York, N. Y., 1944.

<sup>75</sup> Miller, F. A., and Wilkins, C. H., Anal. Chem. 24, 1253, 1952.

<sup>76</sup> Lucchesi, C. A., Offic. Dig. Federation Soc. Paint Technology 30, 212, 1958.

TABLE 37-13 QUALITATIVE TESTS FOR INORGANIC PIGMENTS

<i>Tests and Results (Notes Below Table)</i>	<i>Pigments Present (Nos. in Tables 37-11 &amp; 37-12)</i>
A Action of 4 M HCl, first at room temp, then with moderate heating, and finally at boiling temp with	
1 Evolution of CO <sub>2</sub> (NOTE 1)	7, 13
2 Evolution of H <sub>2</sub> (NOTE 2)	59, 60
3 Evolution of H <sub>2</sub> S (NOTE 3) with the following observation	
a White substance stays white	4
b Yellow substance becomes colorless, dissolves completely or partially	23
c A blue or violet color disappears (colorless residue, unless additional colored substances are present)	20
4 Evolution of H <sub>2</sub> Se (NOTE 3), the red substance partially dissolving	42
5 Evolution of Cl <sub>2</sub> (NOTE 4)	21, 22, 28, 31, 32, 36, 37, 57
6 Substance dissolves completely or almost completely and solution thus obtained is	
a Colorless	3, 5, 7, 8, 9, 13, 17, 57, 59, 60
b Green	21, 22, 31, 32
c Yellow	24, 34, 39, 56
7 The substance does not dissolve or dissolves only partially, while	
a Liquid and residue both colorless	1, 2, 4, 6, 10, 11, 12, 14, 15, 16 20
b Liquid colorless, but residue colored or black	18, 19, 29, 30, 53, 54, 55, 58
c Liquid yellow or orange and residue colorless, colored, or black	25, 26, 35, 36, 37, 38, 40, 41
d Liquid green and residue blue or often a greenish brown	28
B Action of 2 M HOAc, first at room temp, then with moderate heating, finally at boiling temp with	
1 Evolution of CO <sub>2</sub> (NOTE 1)	7, 13
2 Evolution of H <sub>2</sub> S (NOTE 2)	20
3 Substance dissolves completely or at least largely, and the solution is	
a Colorless	3, 5, 7, 13, 60
b Yellow or greenish yellow	22
C Action of 4 M NaOH, first at room temp, then with moderate heating, finally at boiling temp with	
1 Evolution of H <sub>2</sub> (NOTE 2)	59, 60
2 A blue or green pigment color disappears and turns into a brownish shade	18, 28

TABLE 37-13. (Continued)

<i>Tests and Results (Notes Below Table)</i>	<i>Pigments Present</i> (Nos. in Tables 37-11 & 37-12)
3. A blue, green, or violet color, which does not disappear.	20, 30
4. Substance dissolves completely, and the solution is:	
a. Colorless.	3, 5, 7, 8, 59, 60
b. Yellow.	21, 22, 31, 32
5. Substance does not dissolve or at least not completely, while:	
a. Liquid and residue both colorless.	1, 2, 4, 6, 9, 10, 11, 12, 13, 14, 15, 16, 17
b. Liquid colorless but residue colored.	19, 20, 23, 24, 25, 26, 29, 30, 34, 35, 36, 37, 38, 39, 40, 41, 42, 57
c. Liquid colorless but residue gray or black	53, 54, 55, 56, 58
d. Liquid yellow and residue brown.	18, 28
D. Some minutes boiling with 1 M Na <sub>2</sub> CO <sub>3</sub> , cooling, and filtering. The filtrate is:	
1. Colorless or yellow; after adding HCl and then BaCl <sub>2</sub> , white ppt. forms (NOTE 5).	2, 4, 5, 8, 14, 17, 20, 21, 23, 28, 31, 32, 41, 42
2. Colorless; after adding HNO <sub>3</sub> and then a little NH <sub>4</sub> OH or NH <sub>4</sub> NO <sub>3</sub> gives positive phosphate test when heated with excess ammonium molybdate.	55
3. Yellow; after adding H <sub>2</sub> SO <sub>4</sub> , then H <sub>2</sub> O <sub>2</sub> (3%) gives blue-violet color which soon turns green, particularly when hot (NOTE 6).	21, 22, 28, 31, 32
4. Yellow; after adding HCl and then Fe(III) or or Fe(II) salts, gives a blue ppt., or at lower conc. only blue color (NOTE 7).	18, 28
E. After some minutes boiling with ammoniacal (NH <sub>4</sub> ) <sub>2</sub> CO <sub>3</sub> solution and cooling, followed by filtration, the filtrate is:	
1. Colorless and gives zinc test (NOTE 8).	3, 5
2. Yellow after reduction of the chromate gives a positive test for zinc (NOTE 9).	22

NOTE 1. Identified by turbidity which forms in Ba(OH)<sub>2</sub> solution on a glass rod.

NOTE 2. Recognized by its combustibility.

NOTE 3. Recognized by odor; identified by blackening of moistened Pb(OAc)<sub>2</sub> paper.

NOTE 4. Recognized by odor; identified by blue color of moistened KI-starch paper.

NOTE 5. Precipitation or at least strong turbidity at boiling temperature.

NOTE 6. This is a test for chromic acid; test becomes more sensitive in presence of ether, in which blue perchromic acid readily dissolves on shaking.

NOTE 7. This is a test for ferric ferrocyanide; in presence of large quantity of chromate, the latter must be reduced with an excess of a ferrous salt, since otherwise the soluble brown ferric ferrocyanide alone is formed.

NOTE 8. A test for zinc is made by acidifying the ammoniacal filtrate with acetic acid, and then either adding H<sub>2</sub>S or potassium ferrocyanide. A white precipitate in either case indicates the presence of zinc.

NOTE 9. The chromate is reduced by boiling with HCl and alcohol. H<sub>2</sub>S or potassium ferrocyanide should then give a white precipitate if zinc is present.

## IDENTIFICATION OF ORGANIC PIGMENTS

## SPOT TESTS

Several schemes for the identification of organic pigments by means of spot tests have been proposed. One such scheme<sup>77</sup> first divides the pigments into two groups—those soluble in chloroform and those insoluble in chloroform. The spot test is then made on a spot plate by dissolving a small quantity of the unknown in concentrated sulfuric acid. An observation of the color in sulfuric acid, in a water dilution of the acid, and in the water-diluted portion made basic with ammonium hydroxide is made. Comparison of these colors with those tabulated for known organic pigments and confirmatory tests, makes possible the identification of nearly all of the commonly used pigments. A partial reproduction of this scheme is included in a recent book by Payne.<sup>78</sup>

Gardner<sup>79</sup> has included Henlein's scheme for the identification of color lakes and another method based on the work of Weiberg and Smith. A book by Pratt<sup>80</sup> is a thorough treatise on the chemistry and physics of organic pigments. One chapter of this book is devoted to the identification of organic pigments.

## INFRARED METHODS

Infrared spectrophotometry is an especially powerful tool for identifying organic pigments. The absorption spectra of 16 common organic pigments are given in reference<sup>14</sup>; the spectra of organic pigments also may be found in the Encyclopedia of Spectroscopy.<sup>15</sup>

## ANALYSIS OF WHITE AND TINTED PIGMENTS

## GENERAL

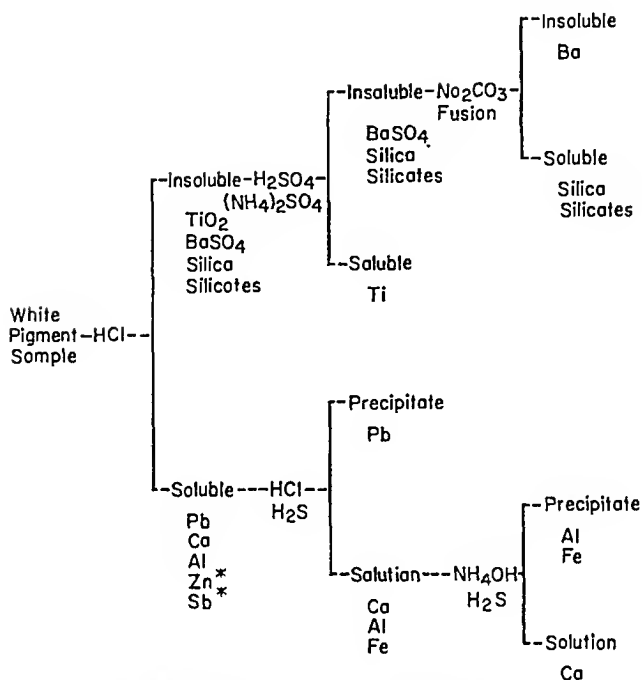
It is possible by means of the qualitative tests given above to determine quite accurately which of the pigments are present in a mixture. However, there are many times, particularly with white pigments, when much time can be saved by proceeding directly with the quantitative analysis. Since the majority of paints are pigmented with white or tinted pigments, the quantitative analysis of this class of pigments will be treated rather completely. The outline of the general procedure used for the complete analysis of a white or tinted pigment will be discussed first and then detailed procedures for each likely component of a white pigment will be given. A flow sheet of the general procedure is shown in Fig. 37.4.

<sup>77</sup> American Cyanamid Company, Identification of Pigments by Spot Testing Bulletin 2-5-12, American Cyanamid Co., Pigments Division, 30 Rockefeller Plaza, New York 20, N. Y., 1957.

<sup>78</sup> Payne, H. F., Organic Coating Technology, vol. II, p. 870, John Wiley and Sons, Inc., New York, N. Y., 1961.

<sup>79</sup> Gardner, H. A., and Sward, G. G., Physical and Chemical Examination of Paints, Varnishes, Lacquers, and Colors, 11th Ed., p. 564, Henry A. Gardner Laboratory, Inc., Bethesda, Md., 1950.

<sup>80</sup> Pratt, L. S., Chemistry and Physics of Organic Pigments, John Wiley and Sons, Inc., New York, N. Y., 1947.



\* Zn And Sb Are Determined On A Separate Sample

FIG. 37.4. Flow Sheet for the Analysis of White Pigments.

### OUTLINE OF GENERAL PROCEDURE

A white pigment is first treated with hydrochloric acid according to Procedure (I) below, and the pigment sample is thereby divided into two portions, a hydrochloric acid-insoluble portion and a hydrochloric acid-soluble portion. The presence or absence of a carbonate or sulfide pigment can be detected visually and by odor as the hydrochloric acid is added to the sample. If there is doubt about the identity of an evolved gas, the procedures given in the notes to Table 37-13 can be used for confirmatory tests. The evolution of carbon dioxide indicates the presence of either or both basic lead carbonate or calcium carbonate. An evolution of sulfide indicates the presence of zinc sulfide, present probably as a component of lithopone. The acid-insoluble portion may contain titanium dioxide; barium sulfate from barytes or lithopone; silica from diatomaceous silica, quartz silica, or basic silicate white lead; and silicates from talc, mica, or clay. The acid-soluble portion may contain calcium from calcium sulfate or calcium carbonate; zinc from zinc sulfide, zinc oxide, or leaded zinc oxide; lead from basic carbonate white lead, basic sulfate white lead, basic silicate white lead, or leaded zinc oxide; antimony from antimony oxide; and aluminum primarily from clays.

The acid-insoluble portion is analyzed for titanium dioxide by Procedure (II). In almost all white pigments (except perhaps those from a white enamel) an insoluble residue will remain after treating the hydrochloric acid-insoluble portion with ammonium sulfate and sulfuric acid. This will contain the extender pigments, such as barium sulfate, silica, and silicates. During the course of this procedure it is frequently possible to detect the presence of barium sulfate, particularly

when it is present in rather large amounts. Barium sulfate is soluble in the hot concentrated mixture of ammonium sulfate-sulfuric acid. However, upon cooling and dilution with water the barium sulfate precipitates. By observing the solution during the dilution one generally can see whether or not an appreciable amount of barium sulfate is present. One of the most reliable ways to identify the sulfuric acid insoluble (extender) fraction is from its infrared spectrum. From the spectrum barium sulfate as well as any siliceous material present can be identified. When barium sulfate is found in the extender portion of the pigment it can be determined by Procedure (III). The silica and silicates are reported as the difference between the total sulfuric acid insoluble portion and the barium sulfate content.

The hydrochloric acid soluble portion will contain the ions of lead, calcium, some aluminum and iron, zinc and antimony if pigments containing these elements were present in the separated pigment sample. When lead is present it may be determined first on the filtrate from the hydrochloric acid treatment by Procedure (IV). If necessary the soluble aluminum and iron may then be determined in the filtrate from the lead determination by Procedure (V) and finally the calcium is determined in the filtrate from the aluminum determination by Procedure (VI). Often it is not necessary to know the acid soluble aluminum and iron content; then calcium is determined on the filtrate from the lead determination.

The zinc and antimony contents of a white pigment are each determined on different samples of the separated pigment by Procedure (VII) and Procedure (VIII) respectively. The sulfate content (Procedure (IX)), the carbonate content (Procedure (X)) and the ignition loss of the pigment (Procedure (XI)) are also determined on different samples of the separated pigment.

### HYDROCHLORIC ACID INSOLUBLE

The procedure given below is taken from Federal Test Method Standard No. 141 Method 5271.<sup>2</sup>

**Procedure (I)**—Weigh to the nearest 0.1 mg. about 1 g. of the pigment into a 250 ml. beaker. Moisten the pigment with a few drops of alcohol, add 40 ml. of 1:1 hydrochloric acid, cover with a watch glass, and boil gently for 5 to 10 minutes. Remove and wash off watch glass.

Evaporate contents of beaker to dryness. This step and the following step may be omitted if soluble silicates are known to be absent.

Heat at about 150°C. for 0.5 or 1 hour to dehydrate the residue. Moisten residue with 4 ml. of concentrated hydrochloric acid.

Dilute contents of beaker to 100 ml. with hot water, boil a few minutes, filter into a 100 ml. beaker, and wash with 100 ml. of hot water. Save filtrate if further analysis is desired.

Ignite paper and residue in a tared crucible. Cool and weigh.

Calculation—

$$\text{Per Cent HCl Insoluble} = \frac{\text{Weight of Residue} \times 100}{\text{Weight of Pigment}}$$

### TITANIUM DIOXIDE

There are two standard procedures for titanium dioxide in common use: the Jones Reductor method and the aluminum reduction method. Both of these procedures are incorporated into ASTM Method D1394-56T. The authors have



found both procedures, as well as the peroxide colorimetric method,<sup>81</sup> to give accurate and reliable results. Because the aluminum reduction procedure is the most rapid and requires the least equipment, it is given below.

**Apparatus.**—Delivery Tube, made of about 4-mm. inside diameter glass tubing bent so that there is a horizontal run of about 6 inches and a vertical drop of about 3 inches at one end, and a vertical drop of about 6 inches at the other end.

**Reagents.** Ammonium Thiocyanate Indicator Solution.—Dissolve 24.5 g. of ammonium thiocyanate in 80 ml. of hot water, filter, bring to room temperature, and dilute to 100 ml. Keep in a well-stoppered, dark-colored bottle.

Ferric Ammonium Sulfate Solution (1 ml. = 0.005 g. Titanium Dioxide).—Dissolve 30.16 g. of fresh ferric ammonium sulfate ( $\text{FeNH}_4(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ ) in 800 ml. of water containing 15 ml. of sulfuric acid. Add 0.1 *N* potassium permanganate solution until a very slight pink color is obtained. Dilute to one liter and mix well. Filter, if cloudy. Standardize using 0.1900 to 0.2100 g. of N.B.S. standard sample No. 154 of titanium dioxide following procedure given below.

**Procedure (II).**—Transfer the hydrochloric acid-insoluble to a 500-ml. Erlenmeyer flask. Add 7 to 9 g. of ammonium sulfate and 20 ml. of concentrated sulfuric acid. Mix well, heat on a hot plate until fumes are evolved, and then over a direct flame until fumes become separate from the liquid portion. Cool and add 120 ml. water and 30 ml. concentrated hydrochloric acid. Bring to a boil and remove from heat.

Insert the short end of the delivery tube into one hole of a two-hole rubber stopper suitable for the Erlenmeyer flask. Insert a glass rod with a slight hook or collar at the bottom end into the other hole of the stopper in such a way that the bottom end will be near the bottom of the flask when the stopper is inserted into the flask. Attach about 1 g. of aluminum foil to the bottom end of the rod by crumpling or coiling the foil around the rod. Insert the stopper carrying the rod with the foil and the delivery tube into the flask in such a way that the foil will be near the bottom of the flask at the same time that the long end of the delivery tube will be near the bottom of a 250-ml. beaker containing about 150 ml. of a saturated solution of sodium bicarbonate.

As soon as the dissolution of aluminum slows down, heat the flask to gentle boiling until the solution of the aluminum is complete, without removing the delivery tube from the sodium bicarbonate solution. Cool to about 60°C. by partial immersion of the flask in cold water. The bicarbonate solution should siphon into the flask during this cooling, giving an atmosphere of carbon dioxide over the reduced titanium solution. Withdraw and wash down the stopper assembly with water.

Add 2 ml. of ammonium thiocyanate indicator solution and titrate immediately with ferric ammonium sulfate solution to a straw-colored end point.

Calculation.—

$$\text{Per Cent TiO}_2 = \frac{A \times B \times 100}{S}$$

where *A* = ml. of ferric ammonium sulfate solution required for titration of sample,

*B* =  $\text{TiO}_2$  equivalent of the ferric ammonium sulfate solution in grams per ml.,  
and

*S* = weight of sample in grams.

<sup>81</sup> Snell, F. D., and Snell, C. T., *Colorimetric Methods of Analysis*, 3rd ed., vol. II, chapter 22, D. Van Nostrand Co., Princeton, N. J., 1949.

iron determination (Procedure (V)) or for the calcium determination (Procedure (VI)).

Boil the filter paper and precipitate with 30 ml. of diluted nitric acid (1:3) until all of the lead sulfide has dissolved, filter, and wash thoroughly with hot water.

To the filtrate add 10 ml. of sulfuric acid (1:1), evaporate until copious fumes of sulfuric acid are evolved. Cool, and add 75 ml. of distilled water and 75 ml. of ethyl alcohol (95%).

Let stand about 1 hour, filter on a weighed Gooch crucible which has been previously ignited. Wash with alcohol diluted with an equal volume of distilled water. Dry, ignite at 600°C., and weigh as lead sulfate.

Calculation.—

$$\text{Per Cent Pb} = \frac{\text{Wt. PbSO}_4 \times 0.6833 \times 100}{\text{Wt. sample in grams}}$$

#### ACID-SOLUBLE ALUMINUM AND IRON

The amount of aluminum and iron present in white pigments is usually small; it would be unusual for the total oxide precipitate to account for more than 1 to 2% of the total pigment. When acid-soluble aluminum is present in amounts considerably greater than this, it is probable that the pigment contains a clay extender. The iron present can be accounted for by impurities in the white pigments and by the use of iron-containing tinting pigments.

It is generally sufficient to determine the total of the aluminum and the iron and report as  $R_2O_3$ . This can be done by precipitation as the hydroxide in the manner outlined below. This is a well-known method and is similar to that given in A.S.T.M. Method D718-45.

*Procedure (V).*—The retained filtrate from the second paragraph of Procedure (IV) is used for this analysis. Boil the solution to remove the hydrogen sulfide. Add bromine water and continue the boiling to remove the bromine. Add methyl red indicator and make the solution basic with ammonium hydroxide.

Filter, wash, ignite and weigh as the oxides of iron and aluminum. Save the filtrate for the determination of calcium.

Calculation.—

$$\text{Per Cent } R_2O_3 = \frac{\text{Wt. of ppt.} \times 100}{\text{Wt. of sample}}$$

#### ACID-SOLUBLE CALCIUM

The acid-soluble calcium can be determined by a procedure based on A.S.T.M. Method D1394-56T which is outlined below. Alternately, the calcium can be determined on the filtrate from the second paragraph of Procedure (IV) by a method involving the use of EDTA. Zinc, if present, is complexed with potassium cyanide before titration with EDTA to the murexide end point. The details of this procedure are given in a recent book by Welcher.<sup>82</sup>

*Procedure (VI).*—The retained filtrate from the second paragraph of either Procedure (IV) or (V) is used for this determination.

Neutralize the solution with ammonium hydroxide or hydrochloric acid. Add

<sup>82</sup> Welcher, F. J., *The Analytical Uses of Ethylenediaminetetraacetic acid*, p. 103, D. Van Nostrand Co., Princeton, N. J., 1958.

10 ml in excess of ammonium hydroxide and pass hydrogen sulfide into the solution for 10 minutes. Let settle and filter into a 600 ml beaker.

Acidify and boil the filtrate to remove the hydrogen sulfide. Add bromine water and boil to remove bromine.

Dilute to 200 ml, neutralize with ammonium hydroxide and add 5 ml in excess. Slowly add 16 ml of saturated ammonium oxalate solution, boil for 5 minutes and keep warm for 1 hour.

Filter and wash the precipitate well with hot water. Place a beaker under the filtering funnel and pierce the filter paper. Wash the precipitate into the beaker with a stream of hot water and then with 40 ml of sulfuric acid (1:4). Save the paper.

Dilute the solution to 200 ml, heat to 90°C and titrate with 0.1 N potassium permanganate. After the end point is reached place the filter paper into the solution and titrate to the end point again to make certain all the oxalate was removed from the paper.

Calculation —

$$\text{Per Cent Ca as CaCO}_3 = \frac{\text{Ml KMnO}_4 \times N \times 0.0500 \times 100}{\text{Weight of sample}}$$

### TOTAL ZINC

Total zinc can be determined by following one of the procedures given in ASTM Method D3456T. However, the authors have found the EDTA procedure given below to be as accurate and more rapid and convenient than the ASTM procedure. This method is based on the published work of Swann and Adams<sup>83</sup> and on a modification suggested by Swann in a private communication.

The EDTA method is based on the reaction of EDTA disodium ethylenediaminetetraacetate, with the zinc ion in solution. The pigment is shaken with an ammoniacal ammonium chloride solution. Zinc pigments with the exception of zinc sulfide are soluble in this solution. The only other pigments soluble in the solution are certain chromate pigments (which do not interfere) and calcium sulfate. If calcium sulfate is present, the calcium is precipitated as the phosphate. The solution is filtered, and the filtrate is titrated with EDTA. If zinc sulfide is present, the pigment is first boiled with hydrochloric acid. Phosphoric acid is added, concentrated ammonium hydroxide is added to make the solution alkaline followed by the ammoniacal ammonium chloride solution. All interfering cations are precipitated by the resulting mixture. The solution is filtered, and the filtrate is titrated with EDTA.

**Reagents.** Buffer Solution—Add 350 ml of ammonium hydroxide (sp gr 0.90) to 54 g of ammonium chloride and dilute to one liter with water.

EDTA, Standard Solution (0.1 M)—Weigh 37.225 g of disodium ethylenediaminetetraacetate, dissolve in water and dilute to 1 liter. Store the solution in a polyethylene or borosilicate glass bottle.

Indicator Mixture.—Mix and grind together 0.2 g of Eriochrome Black T and 100 g of sodium chloride and store in a tightly stoppered bottle.

**Standardization of EDTA**—Weigh to the nearest 0.1 mg triplicate samples of approximately 150 mg of pure zinc metal and transfer to 400 ml beakers. Add 20 ml of hydrochloric acid (1.3), cover with watch glass, and warm until zinc is completely dissolved. Dilute to 200 ml, and neutralize with ammonium hydroxide.

<sup>83</sup> Swann, M. H., and Adams, M. L., *Anal. Chem.* 27, 2005 (1955).

(1:3). A small piece of litmus paper will serve as an indicator. Add 10 ml. of buffer solution, approximately 0.2 g. of indicator mixture and titrate with the EDTA solution to a clear blue color.

Calculate the molarity of the EDTA solution with the equation:

$$\text{Molarity of EDTA Solution} = \frac{\text{Mg. of Zinc}}{\text{Ml. EDTA} \times 65.38}$$

*Procedure (VII)-A (Zinc Sulfide Absent).*—Weigh a sample size sufficient to contain the equivalent of about 150 mg. of zinc and transfer to a 250-ml. Erlenmeyer flask having a 24/40 ground joint.

When calcium sulfate is present add 2 g. of disodium hydrogen phosphate. Add 25 ml. of the buffer solution, stopper the flask, swirl and shake frequently for 15 minutes.

Filter into a 400-ml. beaker. Wash the residue thoroughly with at least 200 ml. of a solution containing 250 ml. of the buffer solution and 10 g. of disodium hydrogen phosphate per liter (when calcium sulfate is absent, the phosphate can be eliminated from the wash water).

Add about 0.2 g. of indicator mixture to the clear solution and titrate with the standard EDTA solution to a clear blue color.

Calculate the zinc content.

*Procedure (VII)-B (Zinc Sulfide Present).*—Weigh a sample size sufficient to contain the equivalent of about 150 mg. of zinc into a 250-ml. beaker. Add 25 ml. of hydrochloric acid (1:1), heat 30 minutes on a hot plate, and finally boil without cover for a few minutes to expel the hydrogen sulfide.

Cool and add in order, 2 ml. of 85% phosphoric acid, 35 ml. of concentrated ammonium hydroxide (slowly), and 25 ml. of the buffer solution. The resulting mixture should be alkaline (pH about 10).

Filter the solution into a 400-ml. beaker and wash with about 200 ml. of a solution containing 250 ml. of the buffer solution and 10 g. of disodium hydrogen phosphate per liter.

Titrate as above and calculate zinc content.

Calculation.—

$$\text{Per Cent ZnO} = \frac{A \times M \times 81.38}{W} \quad \text{Per Cent ZnS} = \frac{A \times M \times 97.44}{W}$$

where  $A$  = ml. of EDTA used for titration of sample,

$M$  = molarity of EDTA, and

$W$  = weight of pigment sample in milligrams.

### ANTIMONY OXIDE

The following method for antimony oxide was taken from Federal Specification AN-TT-A 566 F4a, July 26, 1941.

*Procedure (VIII).*—Weigh to the nearest 0.1 mg. about 1 g. of the pigment into a 500-ml. Erlenmeyer flask.

Add 15 ml. distilled water and 25 ml. concentrated hydrochloric acid, cover with a watch glass and heat in a steam bath for 15 minutes.

Dilute to 250 ml. with distilled water, add 15 ml. sulfuric acid and boil for two minutes.

Cool to 5 to 10°C and titrate with 0.1 *N* potassium permanganate to a pink color which persists for 5 seconds

Calculation —

$$\text{Per Cent Sb}_2\text{O}_3 = \frac{\text{Ml KMnO}_4 \times N \times 0.07289 \times 100}{\text{Wt of sample in grams}}$$

### TOTAL SULFATE

Either lead sulfate or calcium sulfate can be a source of acid soluble sulfate. The method for total sulfate abstracted below is from Federal Test Method Standard No. 141 Method 70c1. A similar method is given in ASTM Method D1301 55.

**Procedure (IX)**—Weigh to the nearest 0.1 mg about 1 g of the pigment into a 400 ml beaker. Moisten with a few drops of alcohol, add 10 ml of bromine water, 10 ml of hydrochloric acid and 3 g of ammonium chloride.

Cover with a watch glass and heat in a steam bath for 5 minutes. Dilute to 200 ml with hot distilled water. Boil for 5 minutes and filter through filter paper. Wash thoroughly with hot water.

Neutralize the clear filtrate in a covered beaker with sodium carbonate. Add 1 g more of sodium carbonate and boil for 10 to 15 minutes. Wash off cover, let settle, filter and wash with hot water containing some of the sodium carbonate.

Redissolve the precipitate in hydrochloric acid (1:1), reprecipitate with sodium carbonate as above. Filter and wash thoroughly with hot water containing some of the sodium carbonate.

Acidify the combined filtrates with hydrochloric acid adding about 1 ml in excess. Boil to expel all bromine and carbon dioxide from the solution. To the clear boiling solution add slowly while stirring 15 ml of 10% barium chloride solution. Let stand on a steam bath for 1 hour or preferably overnight.

Filter on a weighed Gooch crucible previously prepared in the usual manner, wash thoroughly with boiling water, dry, ignite, cool in a desiccator and weigh as barium sulfate.

Calculation —

$$\text{Per Cent Sulfate as BaSO}_4 = \frac{\text{Wt of Ppt} \times 100}{\text{Wt of sample}}$$

This is converted to the proper sulfate by an appropriate factor.

### TOTAL CARBONATE

The source of carbonate in the pigment can be either calcium carbonate or lead carbonate or both. The procedure abstracted below is taken from ASTM Method D1301 55 and can be used to determine the total carbon dioxide evolved from the carbonates present.

**Procedure (X)**—Weigh to the nearest 0.1 mg about 2 g of the pigment and transfer to a clean dry Knorr type carbon dioxide evolution flask. Connect the evolution flask to an absorption train (see NOTE) which has been previously flushed free of carbon dioxide.

Add 100 ml of nitric acid (1:19) through a separatory funnel. When all of the nitric acid has been introduced into the flask, close the stopcock of the funnel. Heat the solution in the flask to gentle boiling and boil for 5 minutes. Turn off the heat and aspirate carbon dioxide free air through the system for 20 minutes.

Remove the absorbing tube from the system, seal, cool in a desiccator and weigh. The increase in weight is carbon dioxide.

Calculation.—

$$\text{Per Cent CO}_2 = \frac{\text{Wt. CO}_2 \times 100}{\text{Wt. of sample}}.$$

NOTE.—A description of a suitable absorption train is given in section 18 of A.S.T.M. Designation C25-47, Standard Methods of Chemical Analysis of Limestone, Quicklime and Hydrated Lime.

### IGNITION LOSS

The ignition loss determination can occasionally be of value as a rough measure of the organic matter adhering to the pigment. However, when pigments are present which lose weight when ignited this determination has little meaning. A commonly used procedure (given below) is taken from A.S.T.M. Method D717-45.

*Procedure (XI).*—Weigh to the nearest 0.1 mg. about 1 g. of the pigment into a porcelain crucible which has been previously ignited, cooled in a desiccator, and weighed. Ignite for about 20 minutes at 900–1000°C. in a muffle furnace. Remove, cool in a desiccator and weigh.

Heat again for 5 minutes to check the loss in weight.

Calculation.—

$$\text{Per Cent Ignition Loss} = \frac{\text{Loss in wt.} \times 100}{\text{Wt. of sample}}.$$

### CALCULATIONS

It is not expected that the total of the results of the analysis of the separated pigment sample will add up to 100%. It is assumed that the principal object of the pigment analysis is not to make a complete analyses of all elements present but to ascertain as nearly as possible the probable pigmentation of the formula.

By combining the results of the analysis with a knowledge of the chemical constituents of the pigments as shown in Tables 37-11 and 37-12 together with the information given in Fig. 37-4, it generally is possible to obtain a fairly accurate estimation of the pigment present.

## ANALYSIS OF COLORED PIGMENTS

### GENERAL

Colored pigments are all those pigments listed in Table 37-12 outside of the black and miscellaneous pigments which will be discussed later. Colored pigments can be used as tinting colors in mixtures of white pigments, in which case they represent a small percentage of the total, usually of the order of 1 or 2%. In other paints the colored pigments may constitute nearly all the pigment and may be tinted with a small amount of white pigment. In many cases of colored pigments, particularly in the case of organic colors, it will be found that only one pigment is present. It also must be recognized that colored pigments may be present with or without extender pigments.

From the color and use of a coating, an experienced analytical paint chemist generally can judge which pigments are likely to be present in the coating. The inexperienced analyst must decide which pigments are present by the use of the

qualitative chemical scheme given in Table 37 13 or by a spectroscopic method. X ray and optical spectrography can be used to detect and determine the elements present. Infrared absorption spectroscopy<sup>14 15</sup> and x ray diffraction can be used to identify which ions, ion combinations, and crystalline forms are present. Once it has been decided which pigment or pigments are present, the analyst must devise a general procedure for analyzing the pigment sample. In this section procedures are given for pure pigments and these procedures should fit into a general scheme devised for a particular sample. Most of the procedures are taken from ASTM or Federal Test Methods Standards and almost always strictly apply only to pigments as raw materials. The authors have found that in general these procedures also apply to the separated pigment portion of a paint except that a given determination on a separated pigment will give a lower result than on the same pigment as a raw material. This is due to adsorbed vehicle in the separated pigment sample. Very useful information on the analysis of pigments may be found in chapters 27, 28 and 29 of reference 14.

#### *YELLOW, ORANGE, RED, AND BROWN PIGMENTS CONTAINING IRON*

The presence of iron in a significant amount indicates that one or more of the following pigments is present: pure yellow iron oxide, pure red iron oxide, pure brown iron oxide, metallic brown, red iron oxide, Venetian Red, raw sienna, burnt sienna, raw umber, burnt umber, and yellow ochre. Deciding which of these pigments is present may not always be possible, however. The usual practice is to carry out as many of the procedures given below as seems necessary. From the results and from a knowledge of the average composition of the various iron containing pigments as shown in Table 37 12, it is possible to estimate the type and quantity of pigment present.

Probably the most common type of iron pigments are the pure oxides which with the exception of pure yellow oxide, contain approximately 98%  $\text{Fe}_2\text{O}_3$ . The pure yellow oxide, because the iron is in the hydrated form, has an iron oxide content of approximately 86%. Since the metallic brown and red iron oxide are ground natural pigments, a considerable range of composition is possible. When calcium sulfate and iron oxide are present in the proportion of 60 to 40 the presence of Venetian Red is quite likely.

The siennas and umbers are earth colors used primarily for tinting purposes. When a significant amount of manganese is found the presence of raw or burnt umber is indicated.

The following ASTM procedures may be helpful in analyzing the pigments in this group: total iron oxide, ASTM Method D50 50, Sec 9 & 10; acid soluble calcium, ASTM Method D50 50, Sec 11 & 12; sulfate soluble in hydrochloric acid, ASTM Method D50 50, Sec 13 & 14, and manganese, ASTM Method D50 50 Sec 17 & 18.

#### *CHROME YELLOW, CHROME ORANGE, AND MOLYBDATE ORANGE*

Methods for the analysis of pigments in this group can be found in ASTM Method D126 50T. Of the determinations presented in D126 50T, the ones of most importance are those for lead chromate, total lead, and molybdenum. Through these determinations and a knowledge of the likely composition of the various pigments, it is possible to roughly approximate the total amount of these pigments present. Although the chrome yellows are essentially lead chromate, the lighter shades contain a considerable amount of lead sulfate. When the pigment is known

to be a chrome yellow, the amount of chromium found is calculated as  $\text{PbCrO}_4$ . The amount of lead found in excess of that necessary for the  $\text{PbCrO}_4$  is calculated as  $\text{PbSO}_4$ , and the total is reported as chrome yellow pigment.

Chrome orange is primarily basic lead chromate. Molybdate oranges are mixtures of lead chromate, lead sulfate, and lead molybdate in various proportions depending on the color.

It is altogether likely that a given pigment will contain mixtures of these pigments. When this is the case, it is only possible to estimate the amounts of the component pigments by determining the lead, chromium, molybdenum and sulfate contents of the total pigment.

### CHROME GREEN

The chrome greens are coprecipitates or mixtures of chrome yellow and iron blue and vary in color from light yellow-green to deep blue-green. The amount of iron blue in the pigment, of course, increases with the depth of color. When chrome green is present in a pigment, some of the iron blue is lost in the pigment washes. The amount so lost can be estimated by an iron determination on the washes. This can be done by evaporating the solvent and igniting the remainder to  $\text{Fe}_2\text{O}_3$ . The iron in this ash can be determined by a standard method.

Methods for the analysis of chrome green can be found in A.S.T.M. Method D126-50T, sections 22-34. In addition, the amount of iron blue present can be estimated by an iron determination. In determining the iron content of chrome green or iron blue, it is necessary to first ignite the pigment so that the iron will become soluble in hydrochloric acid. By multiplying the percentage of iron found by 2.8, the approximate amount of iron blue can be calculated.

### CHROMIUM OXIDE

The chromium in chromium oxide green ( $\text{Cr}_2\text{O}_3$ ) can be determined by the procedure given in A.S.T.M. Method D126-50T, section 38. With the appropriate factor the amount of chrome oxide green in the pigment can be calculated.

### ZINC YELLOW

Zinc yellow is used primarily in corrosion-inhibiting metal primers. Methods for the analysis of zinc yellow are given in A.S.T.M. Method D444-51.

Zinc oxide is often present in combination with zinc yellow. By following the procedure given for the determination of zinc in zinc oxide, the zinc present in zinc yellow will be included. However, from the amount of chromium found the percentage of zinc yellow present can be calculated. The amount of zinc present in this percentage of zinc yellow can be subtracted from the total zinc found and the difference calculated to "free" zinc oxide.

### IRON BLUE AND ULTRAMARINE BLUE

Iron blue pigments are also called "Prussian Blue," Milori Blue, and "Chinese Blue," terms which are significant only insofar as the tint of the blue is concerned. The loss of iron blue in the pigment washes and means for accounting for it have been given above, under Chrome Green. The testing of iron blue as a raw material is given in A.S.T.M. Method D1135-50T, sections 4 to 18. When no other iron-containing pigment is present, the amount of iron blue in pigment mixtures can be estimated by making an iron determination and multiplying the percentage of iron found by 2.8.



of the residue in the crucible as percentage of insoluble mineral matter in the pigment.

### BONE BLACK

Bone black is one of the least frequently encountered pigments shown on the list. The amount present can be estimated through determinations for calcium and phosphate by standard methods. Since calcium can also be present in several other pigments, usually a more reliable estimate of the amount of bone black present can be obtained through a phosphate determination.

### BLACK IRON OXIDE

The amount of black iron oxide in a pigment can be estimated by means of an iron determination and calculation to  $\text{Fe}_3\text{O}_4$ . This method obviously fails when other iron-containing pigments are present. Black iron oxide is encountered only infrequently in pigments, and then it usually is not present in a mixture with other iron pigments.

## OTHER PIGMENTS

### RED LEAD

Red lead is used almost exclusively in corrosion inhibiting primers for iron and steel. It can be used either by itself or in combination with other pigments such as zinc chromate or iron oxide. Methods for the analysis of red lead pigments can be found in Federal Test Method Standard No. 141, Method 7071 or in A.S.T.M. Method D49-44.

Two methods for the determination of true red lead content of red lead pigments have been found useful in the authors' laboratory; these are similar to the Federal and A.S.T.M. procedures but contain some helpful modifications. Procedure *A* given below is useful for pure red lead or for red lead pigment mixtures which contain *no* dark pigments and should be used in appropriate cases because it is the simpler procedure. When dark pigments, such as carbon black or lamp-black, are present Procedure *B* must be used.

**Reagents.** Red Lead Solution.—Dissolve, in a large beaker, 600 g. of sodium acetate and 48 g. of potassium iodide in about 500 ml. of an acetic acid solution (150 ml. of glacial acetic acid and 450 ml. of water). Warm the beaker and contents on a steam bath, stirring occasionally, until a clear solution is obtained. Cool to room temperature and dilute to 1.00 liter with the acetic acid solution, and mix thoroughly.

**Procedure A (Dark Pigments Absent).**—Weigh 1 g. of sample to the nearest 0.1 mg. and brush into a glass mortar.

Add 10 ml. of a mixture of 3 ml. of glacial acetic acid and 7 ml. of methanol. Do not allow pigment to remain in contact with methanol for more than a few minutes. Then add quickly from a graduate 50 ml. of the red lead solution and 30 ml. of water containing 5 or 6 g. of sodium acetate.

Titrate at once with 0.1 *N* sodium thiosulphate solution, keeping the liquid constantly in motion by stirring with the pestle (NOTE 1). When the solution becomes light yellow, rub any undissolved particles until free iodine no longer forms.

Add thiosulphate again until the solution becomes light yellow.

Add starch solution and titrate with the thiosulphate solution to the disappearance of the blue color

Repeat the procedure with no pigment present This blank should be determined once each week due to slow liberation of iodine from red lead solution

**Procedure B (Dark Pigments Are Present)**—Weigh to the nearest 0.1 mg a sample of pigment that will contain about 0.5 g of red lead into a 250 ml beaker

Wet the sample with a small amount of methanol and immediately add 50 ml of the red lead solution Quickly add 20 ml of 0.1 N thiosulphate solution

Warm at 40–50 C for 10 minutes mixing and dispersing the sample very thoroughly during that period

Filter the solution (NOTE 2) and wash well with warm (not hot) water into a 400 ml beaker

Cool add one dropper full of starch solution, and titrate excess thiosulphate with 0.1 N iodine solution to the appearance of the blue starch iodine end point

Repeat this procedure with no pigment present (blank determination)

NOTE 1—The necessity for rapid work at the time the iodine concentration is high especially on hot days cannot be stressed too strongly

NOTE 2—Munktell No. 2 filter paper in a full stemmed funnel is satisfactory

Calculation—For Procedure A

$$\text{Per Cent Pb}_3\text{O}_4 = \frac{(A - B) \times N \times 0.3428 \times 100}{W}$$

where  $A$  = ml of  $\text{Na}_2\text{S}_2\text{O}_3$  solution required for titration of sample,

$B$  = ml of  $\text{Na}_2\text{S}_2\text{O}_3$  solution required for titration of blank,

$N$  = normality of  $\text{Na}_2\text{S}_2\text{O}_3$  solution, and

$W$  = weight of sample taken in grams

For Procedure B

$$\text{Per Cent Pb}_3\text{O}_4 = \frac{(D - E) \times C \times N \times 0.3428 \times 100}{D \times W}$$

where  $C$  = ml of  $\text{Na}_2\text{S}_2\text{O}_3$  used for blank and sample,

$D$  = ml of iodine solution required for titration of blank, and

$E$  = ml of iodine solution required for titration of sample

### GRAPHITE

Graphite is a gray black pigment with a lustrous appearance It is not listed among the black pigments because it is not used for its color value but for the mechanical and chemical properties it imparts to paints Methods for the analysis of pigments extracted from graphite paints may be found in Federal Test Method Standard No. 141, Method 7321

### ALUMINUM

Generally it is sufficient for the analyst to estimate the amount of aluminum pigment present by means of a determination for total aluminum This can be done by a method most convenient for the particular laboratory

### ZINC

Methods for the analysis of zinc dust are to be found in Federal Test Method Standard No. 141, Method 7221 or in ASTM Method D521 50T These methods

are for the analysis of zinc dust as a raw material. Modifications of these methods may be necessary for pigments extracted from paints. Other means for the determination of zinc may also be more convenient for the individual laboratory.

## IDENTIFICATION AND ANALYSIS OF THE THINNER

The definition of the thinner portion of a paint as used in this chapter is taken from A.S.T.M. Method D16-59 which states that a thinner is "the portion of a paint, varnish, lacquer, or printing ink, or related product that volatilizes during the drying process." As described earlier, the thinner portion of a coating is either water or an organic solvent. When the thinner is known to be water, as is the case in the latex paints, all that is necessary is to determine the amount of water in the total coating by the procedure given on page 1619. When the thinner is an organic solvent, an analysis is made on the thinner isolated from the total coating by the procedure given on page 1623.

Reference has been made to publications in which binders were classified and identified by means of solubility tests (page 1639). While this method of identification of resins has its limitations, it is nevertheless very useful upon occasion. Conversely, when the binder portion of the vehicle has been identified, the types of solvents present can usually be predicted. The types of solvents in general use by the coating industry are outlined in Chapter 6 of reference <sup>84</sup>.

Some examples of commonly used solvents classified according to chemical types are given in Table 37-14. A more complete list of the solvents used by the paint industry is given in the solvents section of the Raw Material Index.<sup>72</sup> It must be understood that these solvents are not chemically pure materials. For instance VM&P naphtha and mineral spirits are listed as aliphatic materials although considerable amounts of aromatic and naphthenic hydrocarbons are present. Because of their low cost, the hydrocarbons are used whenever their solvent power is sufficient for the intended purpose. Most paint and varnishes contain hydrocarbons as their main or sole solvent. In addition, the hydrocarbons are used as diluents in lacquer formulations. The oxygenated solvents, being polar compounds, are better solvents for the more polar film-forming materials, such as the cellulose, urea- and melamine-formaldehyde resins, acrylic resins and vinyls. The solvents listed under "other types" are encountered infrequently, principally because of their high cost.

The identification and analysis of solvents by chemical methods has been described in considerable detail by Kappelmeier.<sup>85</sup> Snell and Biffin<sup>74</sup> and Hanson<sup>5</sup> likewise have presented methods for the qualitative and quantitative analysis of solvents by non-instrumental methods. However, in the author's laboratory, the analysis of solvents is performed with the aid of infrared spectrophotometry and gas chromatography. The general composition of the thinner is ascertained from its infrared spectrum, and when necessary, a more detailed analysis is obtained by subjecting the thinner to gas chromatography.<sup>86,87</sup> The infrared spectra of 22

<sup>84</sup> Payne, H. F., *Organic Coatings Technology*, Vol. I, Chapter 6, John Wiley and Sons, Inc., New York, N. Y., 1954.

<sup>85</sup> Kappelmeier, C. P. A., *op. cit.*, p. 231.

<sup>86</sup> Esposito, G. G., *The Application of Temperature Programmed Gas Chromatography to the Analysis of Lacquer Solvents and Thinners*, U. S. Dept. of Commerce, O.T.S. Dept. CCL97, Oct. 7, 1960.

<sup>87</sup> Crippen, R. C., and Emmerling, J., *Offic. Dig. Federation Soc. Paint Technology*, 32, 1517, 1960.

TABLE 37 14 THINNERS USED IN SOLVENT COATINGS

## HYDROCARBON SOLVENTS

Aliphatic	Aromatic
Mineral Spirits	Toluene
VM&P Naphtha	Xylene
Hexane	High Flash Naphtha
C 8 Hydrocarbon Solvent	High Solvency Naphtha
Naphthenic	
Cyclohexane	

## OXYGENATED SOLVENTS

Alcohols	Ether Alcohol
Methyl Alcohol	Methyl Cellosolve *
Ethyl Alcohol	Cellosolve *
Isopropyl Alcohol	Butyl Cellosolve *
n Butyl Alcohol	Carbitol *
Isooctyl Alcohol	Butyl Carbitol *
Esters	Ketones
Ethyl Acetate	Acetone
Isopropyl Acetate	Cyclohexanone
n Butyl Acetate	Isophorone
sec Amyl Acetate	Methyl Ethyl Ketone
Methylamyl Acetate	Methyl Isobutyl Ketone
Ether Alcohol Ester	Methyl Isoamyl Ketone
Cellosolve Acetate *	Ethyl Amyl Ketone
Butyl Cellosolve Acetate *	Furans
	Tetrahydrofuran

## OTHER SOLVENT TYPES

Chlorinated Hydrocarbons	Others
Methylene Chloride	2 Nitropropane
Perchloroethylene	Dimethylformamide

\* Registered Trademark Union Carbide Corporation

thinner materials may be found in the Encyclopedia of Spectroscopy<sup>15</sup> Similar spectra also may be found in reference <sup>14</sup>

## EXAMPLE OF COMPLETE ANALYSIS OF A SURFACE COATING

## GENERAL

This section is included in order to illustrate how the information in this chapter may be used to analyze a paint product. It is assumed that a can containing a coating was received with a request for a complete analysis. The steps which were taken in the analysis of this unknown are given below along with the Sections in which the appropriate procedures can be found.

## ANALYSIS

**Preliminary Inspection (Page 1617).**—The label stated that the coating was a "flat white baking enamel" for general industrial use; no label analysis was given. From its odor, it was obvious that the sample was a solvent type coating.

**Determination of the Nonvolatile Matter (Page 1618).**—The nonvolatile matter of the total paint was found to be 59.3%.

**Separations (Page 1621).**—The following separations gave the results indicated:

<i>Test</i>	<i>Result</i>
Determination and Separation of Pigment	38.6%
Isolation of Vehicle by Supercentrifuge	—
Isolation of Thinner by Vacuum Stripping	—
Isolation of Binder by Supercentrifuge	—

**Calculation of Primary Composition (Page 1625).**—From the percentage of nonvolatile matter and the percentage of pigment obtained above, the primary composition of the total paint was calculated to be:

38.6%	Pigment
20.7	Binder
40.7	Thinner
<hr/>	
100.0%	Total

**Identification of the Binder (Page 1627).**—The isolated binder was identified by infrared and chemical methods. By following the infrared scheme given in Table 37-1, the presence of an alkyd resin and a melamine resin was indicated. By comparing the spectrum of the binder with Spectra Nos. 1 and 5 of the section on Infrared Spectra, the presence of an alkyd-melamine mixture was fairly well established. Qualitative and spot tests given in Table 37-3 were applied and positive tests for nitrogen, formaldehyde, *o*-phthalate, and melamine were obtained. Other spot tests gave negative results, thus corroborating the infrared data.

**Analysis of the Vehicle (Page 1641).**—Having established that the binder was a melamine-alkyd blend, the isolated vehicle was analyzed according to the procedures on page 1663. From the infrared spectrum of the binder, the melamine-formaldehyde resin content was calculated to be 33% and the alkyd resin content 67% by the method referred to on page 1663. A value of 33% melamine also was obtained by determining the nitrogen content of the vehicle by the procedure given on page 1663. The melamine content could have been obtained by the acid hydrolysis procedure given on page 1665. The total vehicle was then saponified by the methods given on page 1664 and the following results were obtained:

<i>Alkyd Fraction</i>		<i>Identification</i>
Dicarboxylic Acids	40.8%	<i>o</i> -Phthalic
Oil Acids	41.7	Dehydrated Castor Type
Polyhydric Alcohol	24.1	Glycerol
<hr/>		
Total Uncombined	106.6%	
Water Loss	7.5	
<hr/>		
	99.1%	

analysis, the titanium pigment is obtained by dividing the "free"  $\text{TiO}_2$  by 0.98; thus,  $41.1/0.98 = 41.9\%$  titanium pigment.

4. Again as shown in Table 37-11, barium sulfate pigments, such as Barytes, contain 98%  $\text{BaSO}_4$ ; thus,  $23.0/0.98 = 23.5\%$  Barytes.
5. Commercial silicates, such as Talc, are generally assumed to be 85% hydrochloric acid insoluble; thus,  $16.1/0.85 = 18.9\%$  Talc.
6. Thus, the most probable composition is as follows:

<i>Pigment Component</i>	<i>Calculated Result</i>	<i>Normalized Result</i>
Titanium-Calcium Pigment	15.3%	15.3%
Titanium Pigment	41.9	42.1
Barytes	23.5	23.6
Talc	18.9	19.0
	<hr/>	<hr/>
	99.6%	100.0%

*Analysis of the Thinner (Page 1703).*—The solvent was examined by infrared spectrophotometry and analyzed by gas chromatography. The following composition was obtained:

C-8 Hydrocarbons	47%
Xylenes	43
Butanol	10
	<hr/>
	100%

### PRESENTATION OF THE DATA

The composition of the flat white baking enamel may be reported as follows:

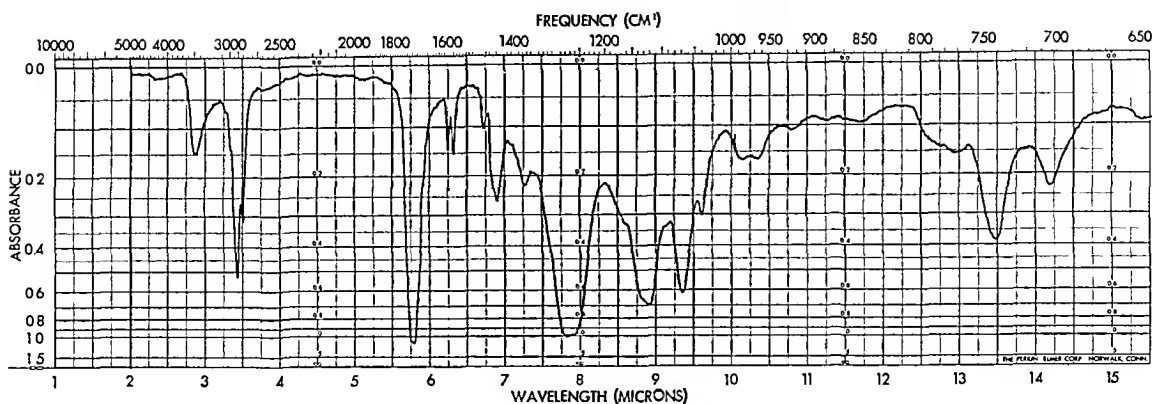
38.6%	Pigment	
	Titanium Dioxide Pigment	42.1%
	Titanium-Calcium Pigment	15.3
	Barytes	23.6
	Talc	19.0
		<hr/>
		100.0%
20.7%	Binder	
	Melamine Formaldehyde Resin	33%
	Alkyd Resin *	67
		<hr/>
		100%
40.7%	Thinner	
<hr/>		
100.0%	C-8 Hydrocarbons	47%
	Xylene	43
	Butanol	10
		<hr/>
		100%

\* Composition of Alkyd Resin.

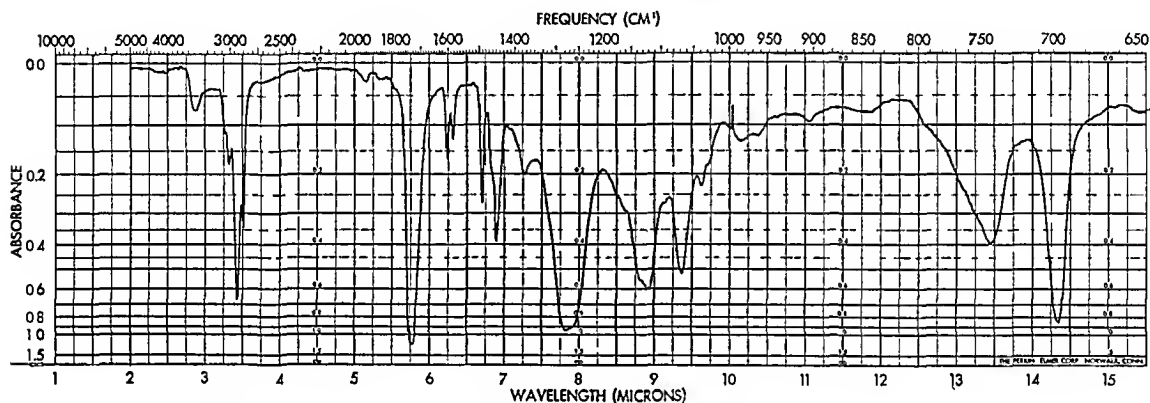
<i>Uncombined</i>		<i>Combined</i>	
Phthalic Anhydride	41.2%	Glyceryl Phthalate	55.7%
Dehydrated Castor Oil Acids	42.1	Dehydrated Castor Oil	44.3
Glycerol	24.2		
	<hr/>		<hr/>
	107.5		100.0%
Water Loss	7.5		
	<hr/>		
	100.0%		

### INFRARED SPECTRA

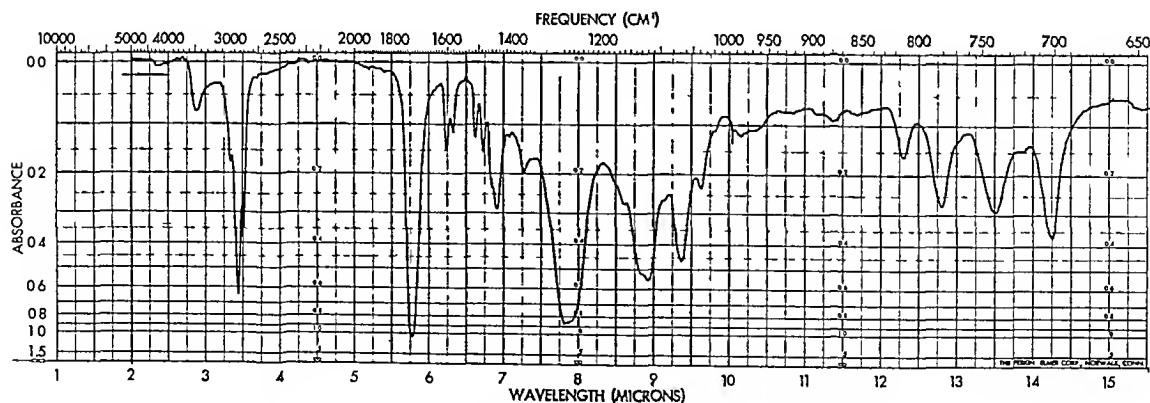
Included in this section are thirty nine infrared absorption spectra useful in the analysis of paint varnish and lacquer



Spectrum No. 1. Linseed Glyceryl Phthalate (Film).

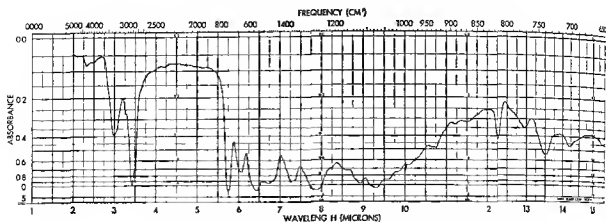


Spectrum No. 2. Styrenated Soya Tung Glyceryl Phthalate (Film).

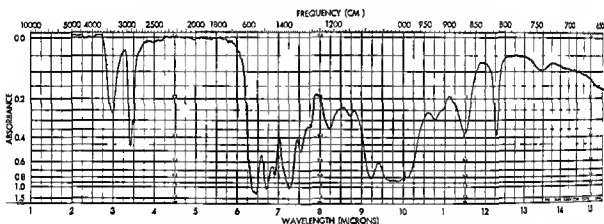


Spectrum No. 3. Vinyl Toluenedated Soya Tung Glyceryl Phthalate (Film).

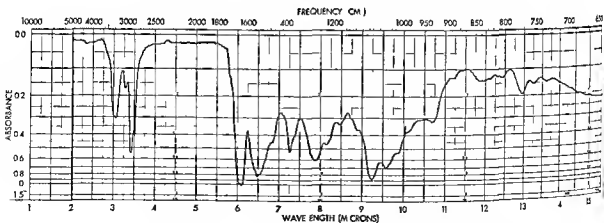




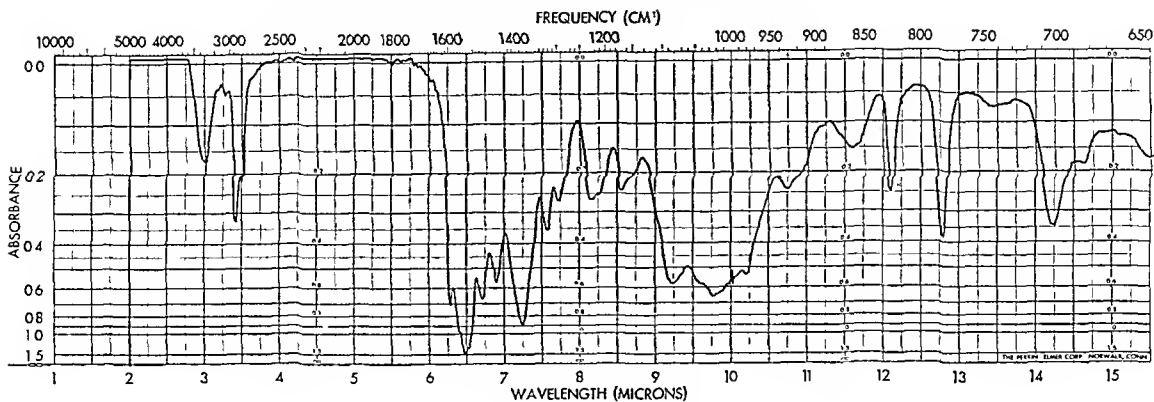
Spectrum No 4 Alkyd Melamine Urea Blend (Film)



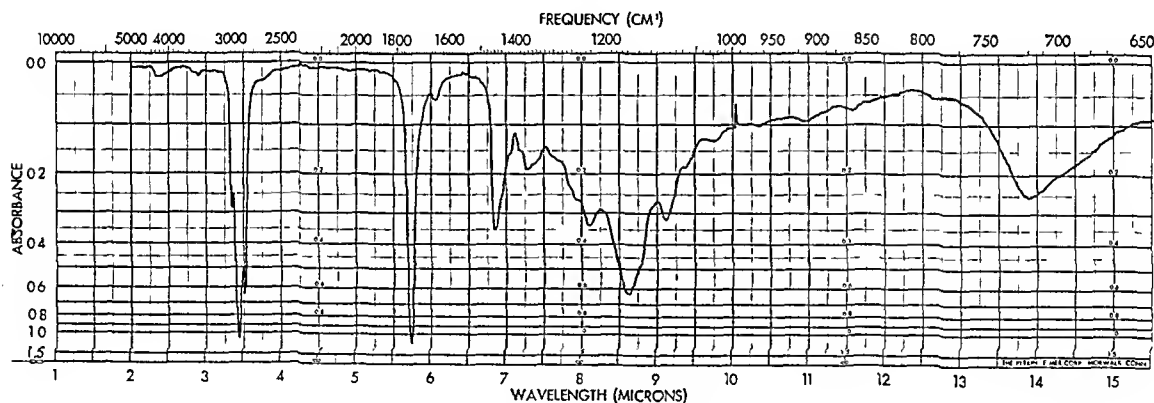
Spectrum No 5 Melamine Formaldehyde n Butylated (Film)



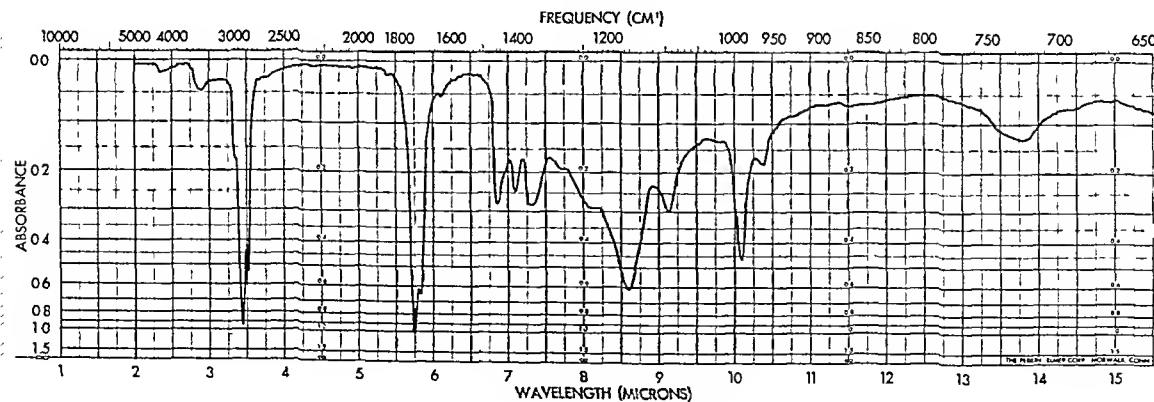
Spectrum No 6 Urea Formaldehyde n Butylated (Film)



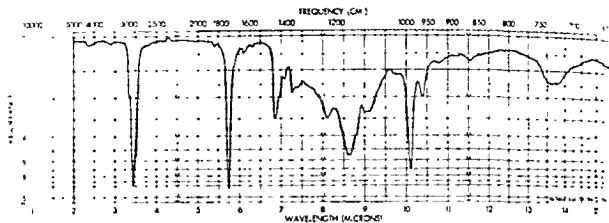
Spectrum No. 7. Benzoguanamine-Formaldehyde (Film).



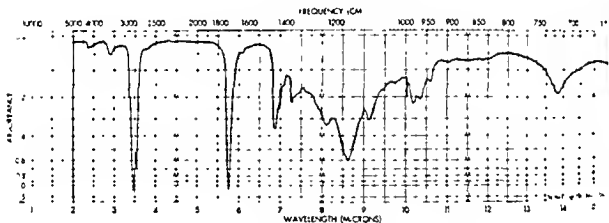
Spectrum No. 8. Linseed Oil, Raw (Liquid).



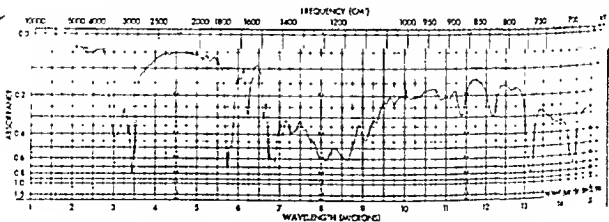
Spectrum No. 9. Oiticica Oil (Liquid).



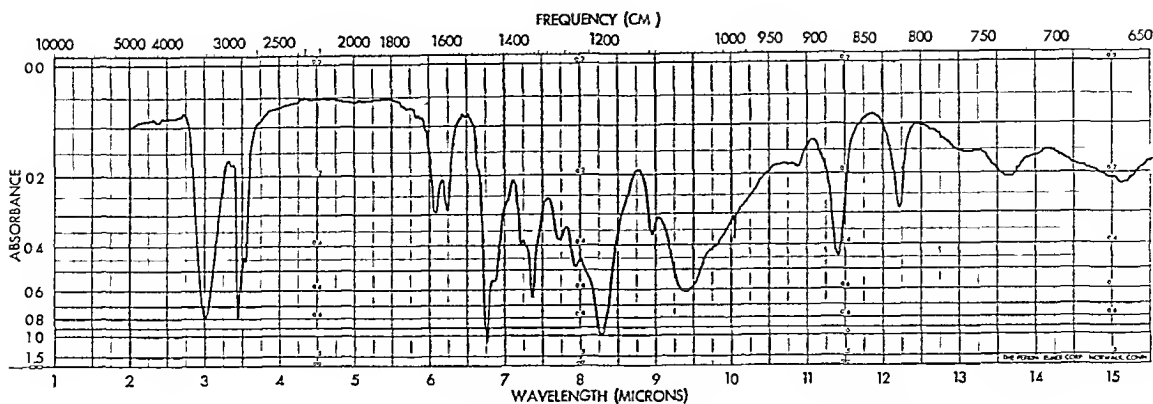
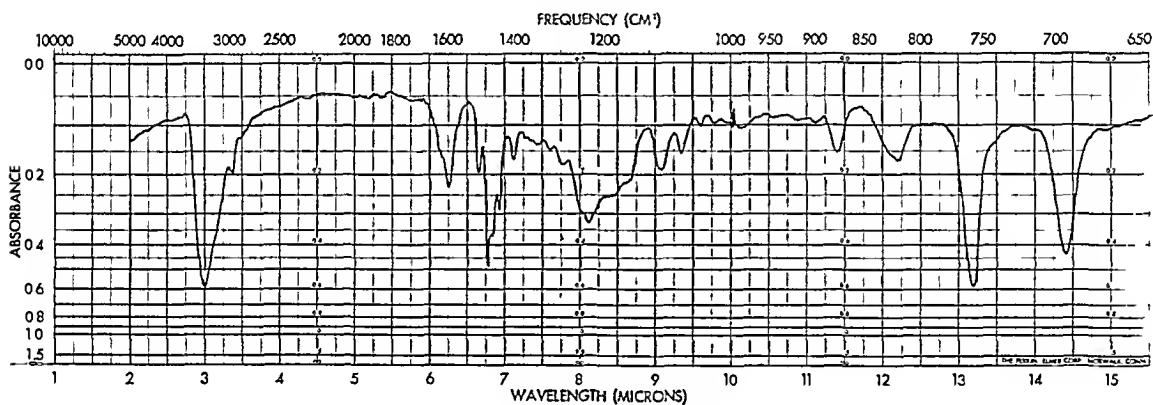
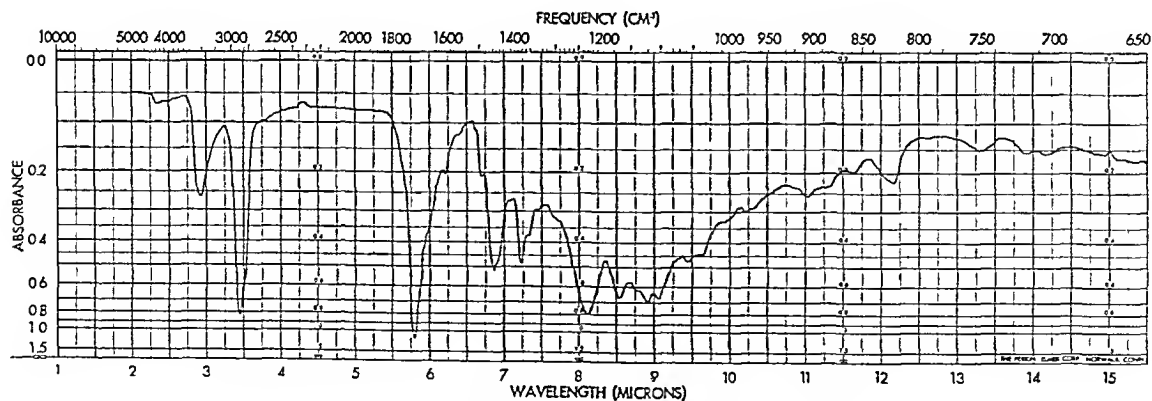
Spectrum No 10 Tung Oil (liquid)



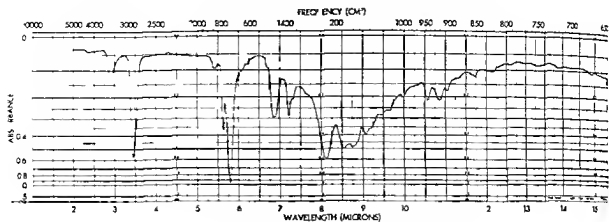
Spectrum No 11 Castor Oil, Dehydrated (liquid).



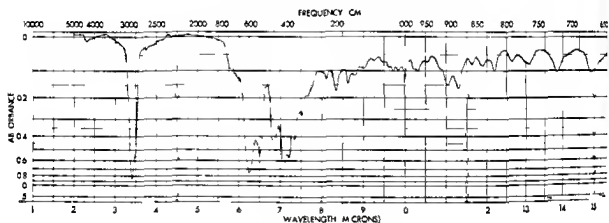
Spectrum No 12 Phenolic Modified Linseed Oil Varnish (film)

Spectrum No. 13. *p*-*tert*-Butylphenol-Formaldehyde (1.4 mg. in KBr).Spectrum No. 14. *p*-Phenylphenol-Formaldehyde (1.2 mg. in KBr).

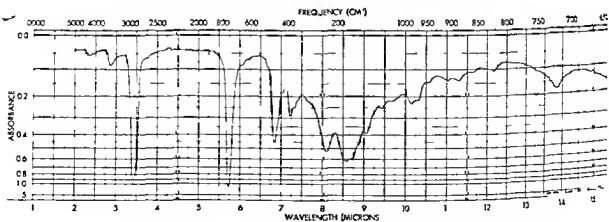
Spectrum No. 15. Glyceryl Ester of Rosin (Ester Gum) (Film).



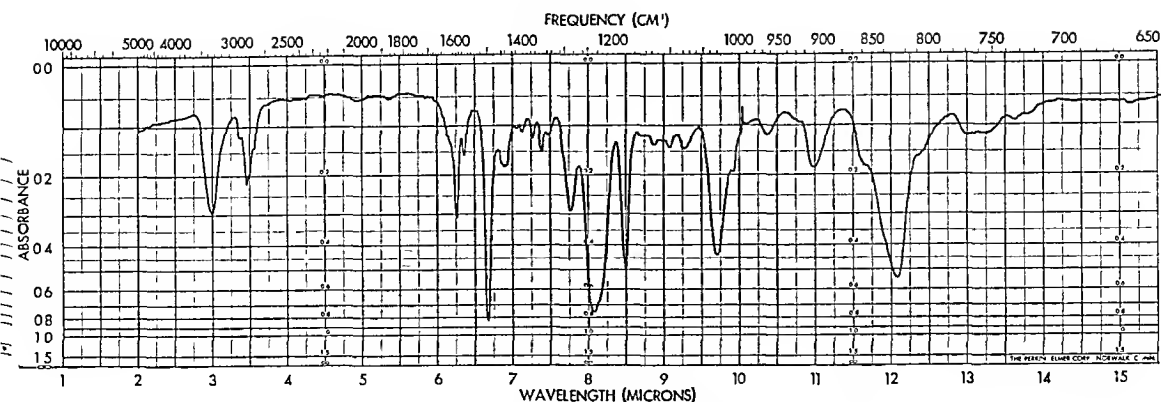
Spectrum No 16 Maltic Rosin Ester (Film)



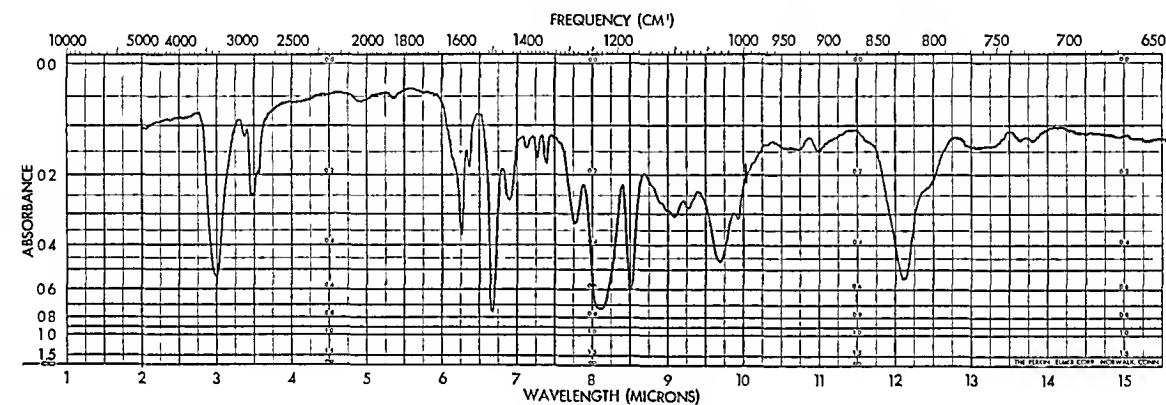
Spectrum No 17 Zinc Resinate (Film)



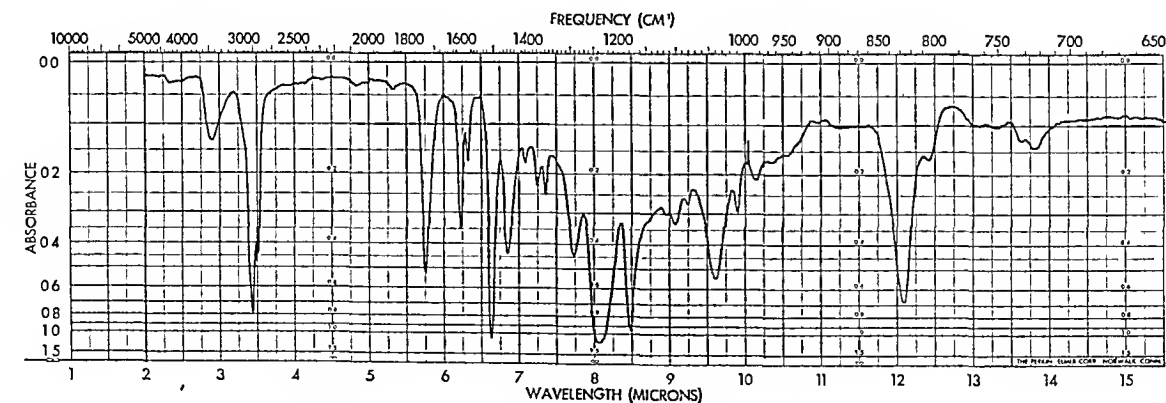
Spectrum No 18 Pentaerythritol Dehydrated Castor Oil Rosin Varnish (Film)



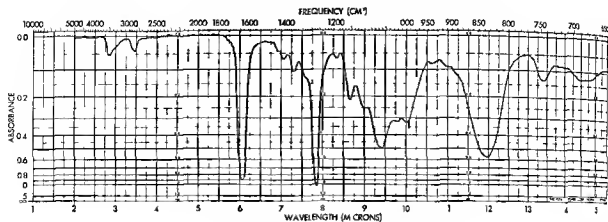
Spectrum No. 19. Bisphenol Type Epoxide with Epoxide Equivalent of 200.



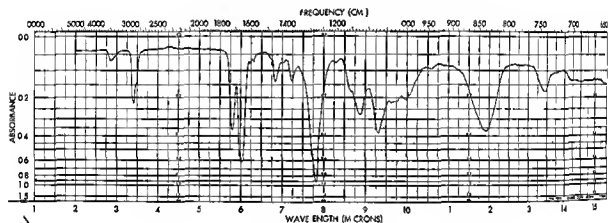
Spectrum No. 20. Bisphenol Type Epoxide with Epoxide Equivalent of 500.



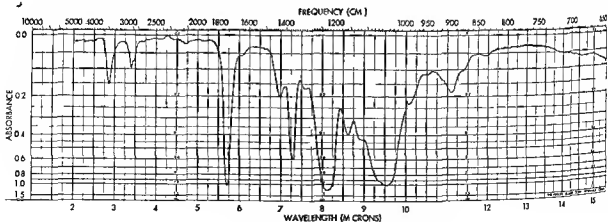
Spectrum No. 21. Epoxide Ester of Castor Oil (Film).



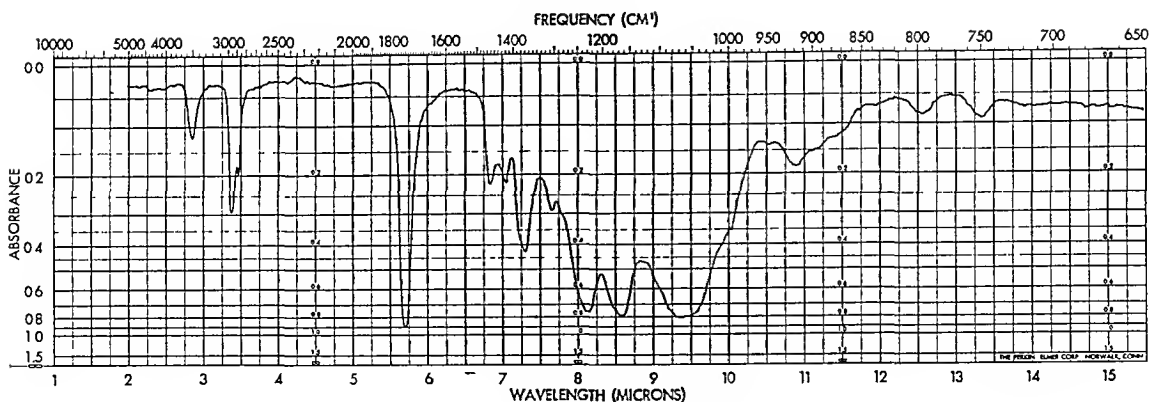
Spectrum No 22 Cellulose Nitrate (Film)



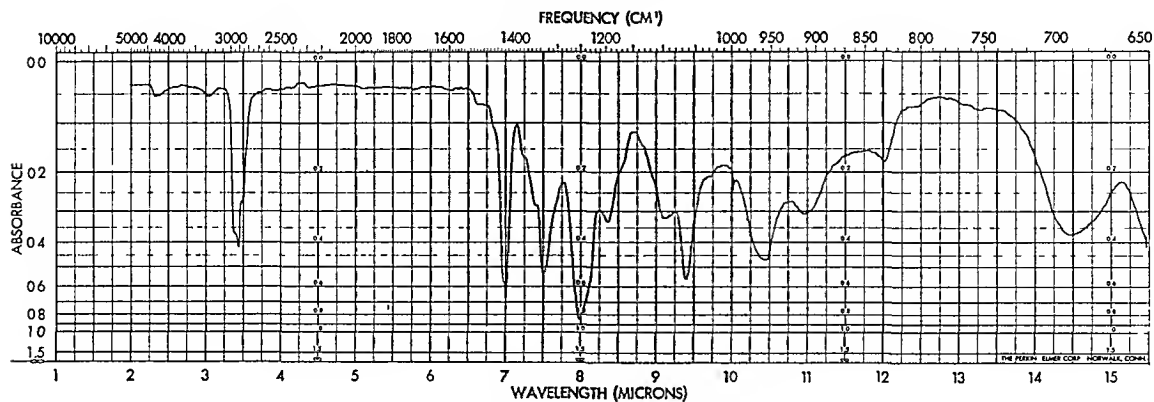
Spectrum No 23 Cellulose Nitrate Phthalate Ester Plasticized (Film)



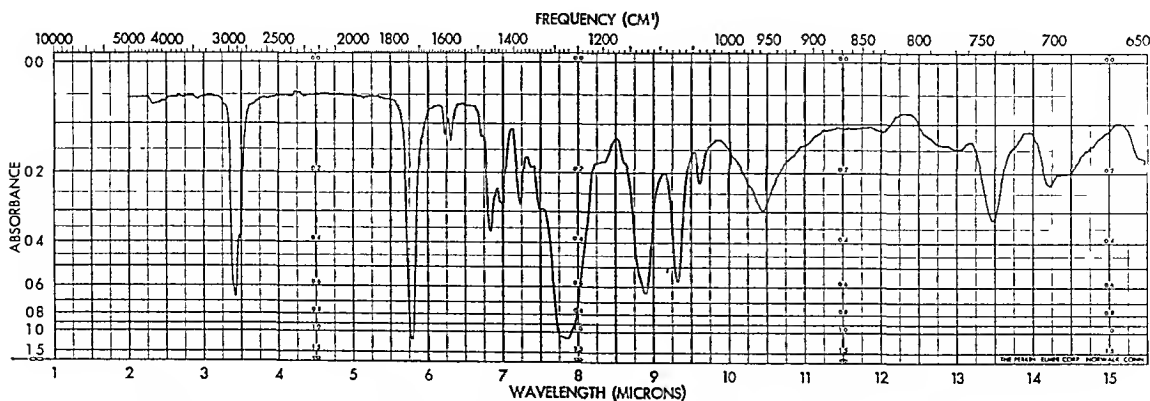
Spectrum No 24 Cellulose Acetate (Film)



Spectrum No. 25. Cellulose Acetate-Butyrate (Film).

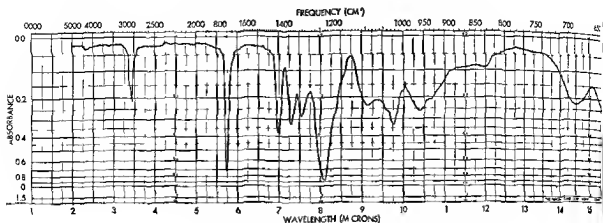


Spectrum No. 26. Poly(Vinyl Chloride) (Film).

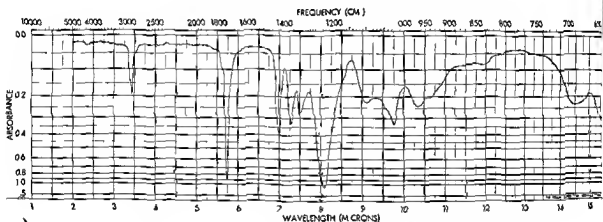


Spectrum No. 27. Poly(Vinyl Chloride), Phthalate Ester Plasticized (Film).

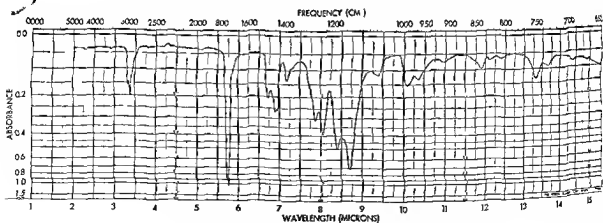




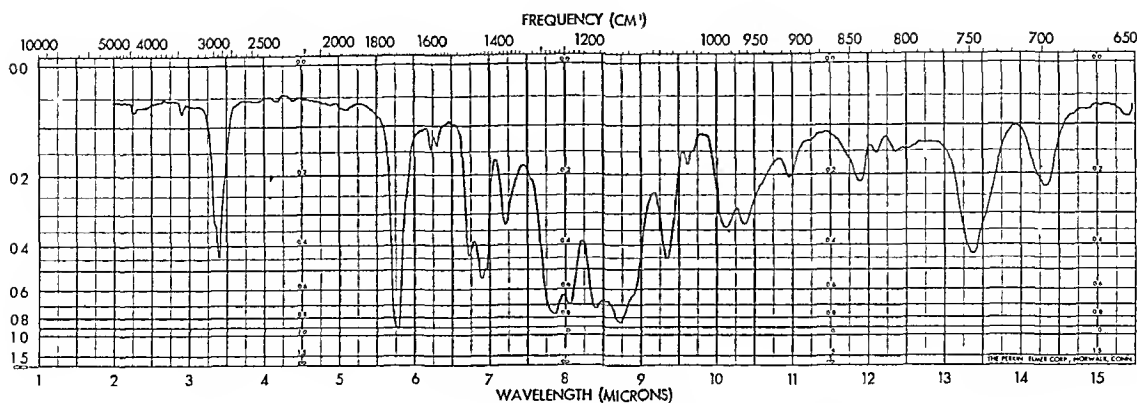
Spectrum No 28 Poly(Vinyl Chloride Acetate) (Film)



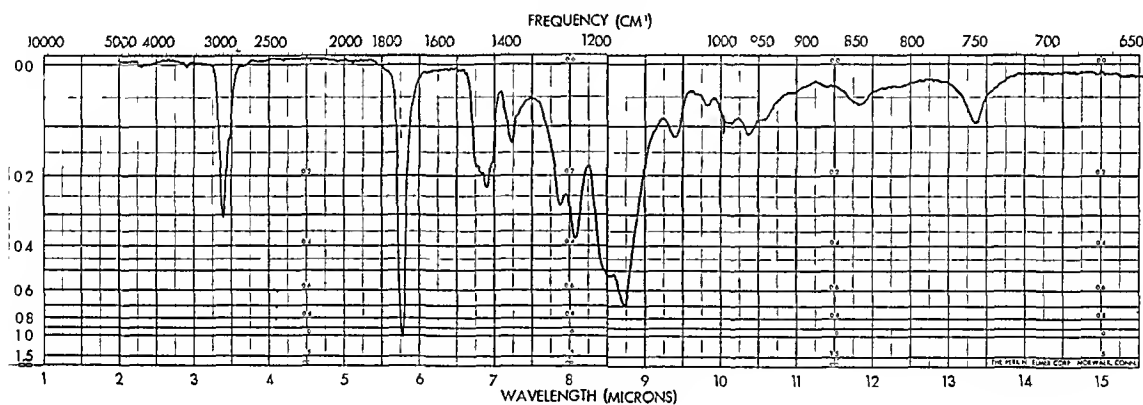
Spectrum No 29 Poly(Vinyl Chloride Acetate Maleate) (1% Maleate) (Film)



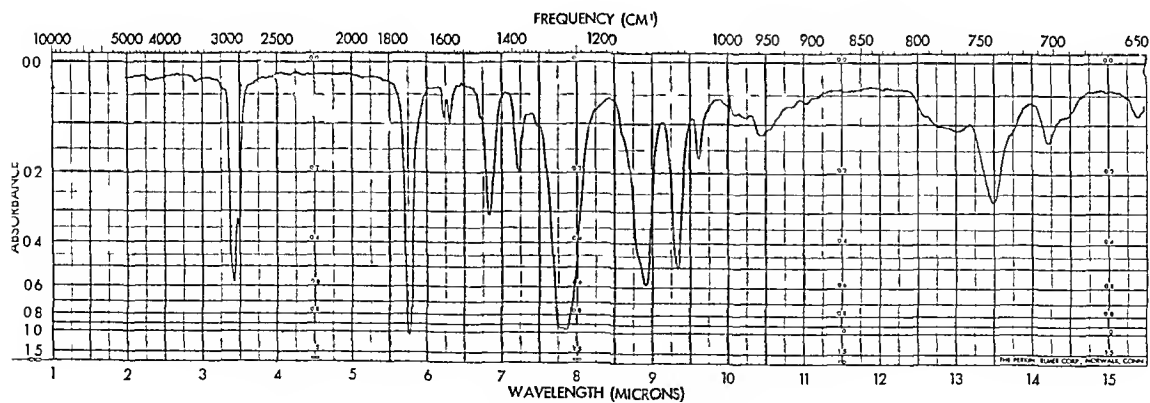
Spectrum No 30 Poly(Methyl Methacrylate) (Film)



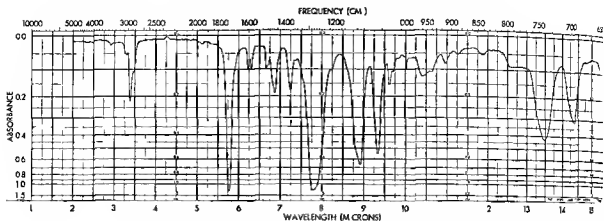
Spectrum No. 31. Poly(Methyl Methacrylate), Phthalate Ester Plasticized (Film).



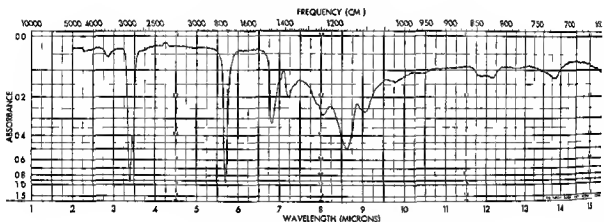
Spectrum No. 32. Poly(Methyl Methacrylate-Butyl Methacrylate) (Film).



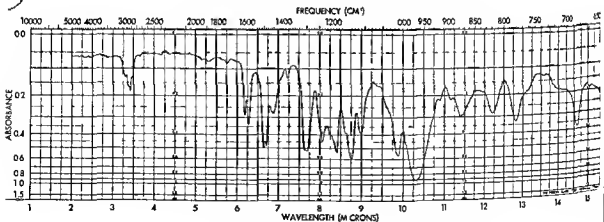
Spectrum No. 33. Di(2-ethylhexyl) Phthalate (Liquid).



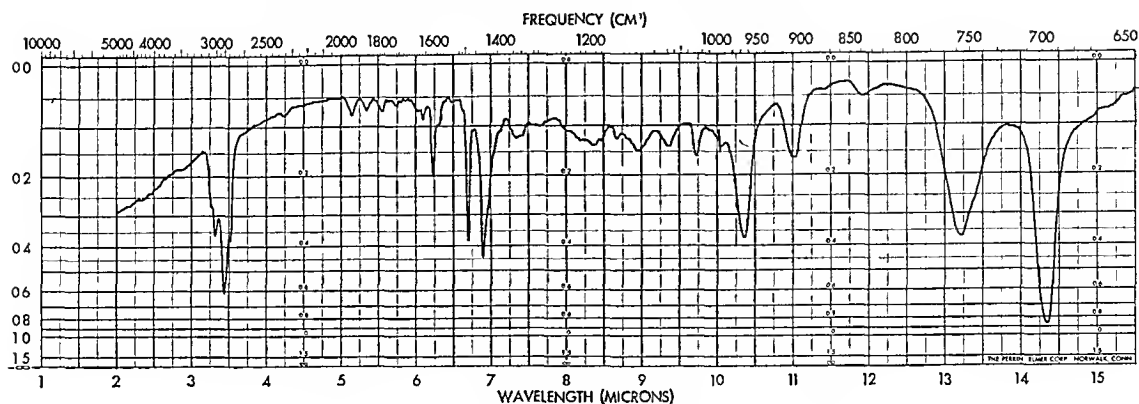
Spectrum No 34 Butyl Benzyl Phthalate (Liquid)



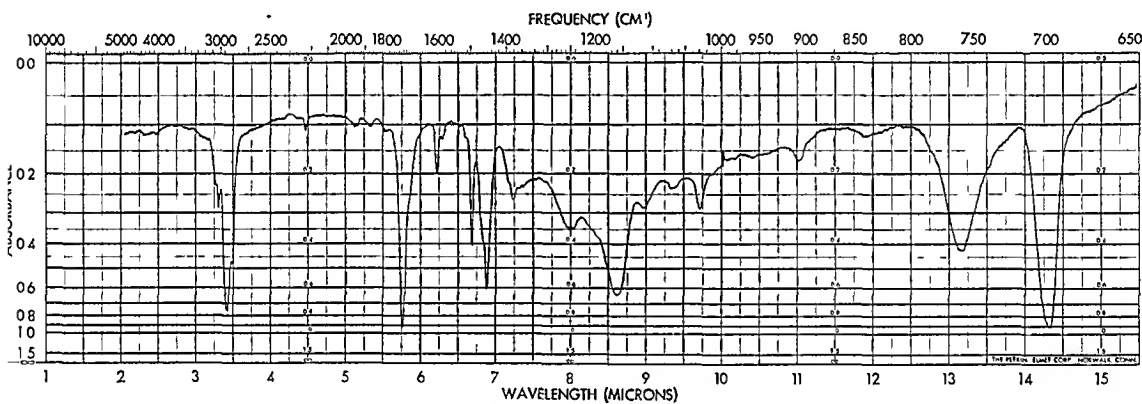
Spectrum No 35 Epoxidized Soya Oil (Liquid)



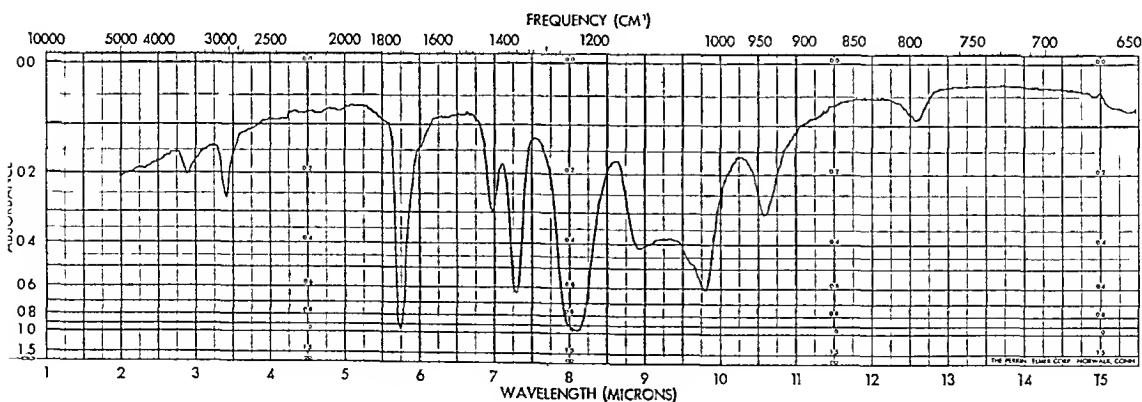
Spectrum No 36 Tricresyl Phosphate (Liquid)



Spectrum No. 37. Poly(Styrene-Butadiene) (Film on AgCl).



Spectrum No. 38. Styrene-Acrylonitrile-Acrylate Terpolymer (Film on AgCl).



Spectrum No. 39. Poly(Vinyl Acetate) (Film on AgCl).

# ANALYSIS OF WOOD

## WATER SOLUBILITY OF WOOD<sup>1,2</sup>

The water solubility of wood is usually determined after extraction with organic solvents, such as alcohol or alcohol-benzene. The extract includes organic salts, sugars, cyclitols, gums, pectin-like materials, and galactans and, if not previously extracted with alcohol, a portion of the tannins and pigments in the wood. Hot water hydrolyzes polysaccharidic and some other components, and increases their solubility. This method is standardized as ASTM D1110 and TAPPI T 1 m-59.

**Apparatus.** For Cold-Water Solubility.—Beaker, 400-ml., and stirring rod.

For Hot-Water Solubility.—Erlenmeyer flask, 200-ml., with reflux condenser, and boiling water bath with its level maintained constant at above the 100-ml. level in the flask.

**Filtering Equipment.**—Crucible, Alundum, RA 98; or fritted glass, medium porosity; with a glass-stoppered weighing bottle, and a suction filter flask with either a rubber flange or a funnel and rubber flange for the crucible.

**Test Sample.**—In accordance with TAPPI Standard T 11 m (page 1734), prepare a representative sample of 40/60 mesh (0.25 to 0.40 mm. diam.) air-dried sawdust, and determine its moisture content. At least 4 g. are required for each solubility determination in duplicate.

**Cold-Water Solubility Procedure.**—From the air-dry sample, weigh to the nearest mg. a specimen which is the equivalent of  $2 \pm 0.1$  g. of moisture-free wood. Place it in a 400-ml. beaker, and cover with 300 ml. of distilled water. Let this mixture digest at a temperature of  $23 \pm 2^\circ\text{C}$ ., with frequent stirring for 48 hours. Transfer the material to a tared filtering crucible, wash with cold distilled water, and dry to constant weight at  $105 \pm 3^\circ\text{C}$ . Drying usually requires approximately 4 hours. Place the crucible in a tared stoppered weighing bottle and cool in a desiccator over concentrated sulfuric acid. Momentarily open the stopper to let in the air and weigh. Calculate the weight of the moisture-free material dissolved.

**Hot-Water Solubility Procedure.**—From the air-dry sample, weigh to the nearest mg. of specimen which is the equivalent of  $2 \pm 0.1$  g. of moisture-free wood. Transfer the specimen to the 200-ml. Erlenmeyer flask in the boiling water bath, add 100 ml. of distilled water, and attach the reflux condenser. Digest for 3 hours, then transfer the contents of the flask to a tared filtering crucible, wash with hot water, and dry to constant weight at  $105 \pm 3^\circ\text{C}$ . Place the crucible and contents in the stoppered weighing bottle, cool in a desiccator over concentrated  $\text{H}_2\text{SO}_4$ . Momentarily open the stopper to let in the air and weigh. Calculate the weight of the moisture-free material dissolved.

**Report.**—Report the amount soluble in cold, or in hot water, to the nearest 0.1

<sup>1</sup> Schorger, A. W., *Chemistry of Cellulose and Wood*, McGraw-Hill, New York, p. 506, 1926.

<sup>2</sup> Wise, Louis E., and Jahn, Edwin C., *Wood Chemistry*, 2nd Ed., esp. Vol I, Part 3, Reinhold, New York, 1952.

per cent based on the moisture free wood and record the equivalent screen mesh if other than 40/60

### METHOXYL GROUPS IN WOOD

The principle of the method is the same as that in the original method of Zeisel<sup>3</sup> except that the methyl iodide is collected in an acetic acid solution of potassium acetate containing bromine. The following reactions then occur<sup>4</sup>

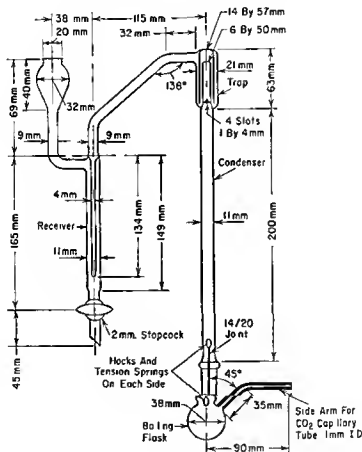
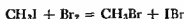


FIG. 38.1 Recommended Methoxyl Apparatus

The iodic acid is determined by titration of iodine liberated by the reaction  $\text{HIO}_3 + 5\text{HI} = 3\text{I}_2 + 3\text{H}_2\text{O}$

This method is standardized as TAPPI T 2 m 60

**Apparatus**—Several forms of apparatus have been used for this determination with satisfactory results. The form shown in Fig. 38.1 is recommended. It consists

<sup>3</sup> Zeisel S, Monatsh. 6, 989 1885 7, 406 1886

<sup>4</sup> Viebock, F., and Schwappach A. Ber., 63, 2818-23 1930

of a reaction flask with side arm for admission of carbon dioxide, an air condenser with a trap, and a receiver. The reaction flask is heated by immersion in an oil bath equipped with a heating device, preferably electrical, so that the bath can be maintained at 145° to 150°C. Figure 38-2 depicts an older methoxyl apparatus that is no longer standard, but is still in use.

**Carbon Dioxide Feeder.**—The carbon dioxide is passed to the flask through a bubble counter and a dry trap, and then through a pressure regulator consisting of a glass tee whose vertical arm extends almost to the bottom of a 10-in. column of water. A screw clamp is attached to the thin-walled rubber tubing connecting the horizontal arm of the tee with the boiling flask. This arrangement permits regulation of the flow of gas and allows any excess gas to escape.

**Reagents. Phosphorus Slurry.**—Add about 0.06 g. of red phosphorus to 100 ml. of water. Shake well before using.

**Potassium Acetate Solution.**—Dissolve 100 g. of anhydrous crystals in 1 liter of a solution containing 900 ml. of glacial acetic acid and 100 ml. of acetic anhydride.

**Bromine Solution.**—Dissolve 5 ml. of bromine in 145 ml. of the potassium acetate solution. Prepare the bromine solution fresh daily in a hood to remove the bromine vapors.

**Propionic Anhydride, Pure.**

**Gelatin Capsules**, containing very little methoxyl and large enough to hold a 50- to 60-mg. specimen.<sup>5</sup>

**Hydriodic Acid (57% sp. gr. 1.70).**—Hydriodic acid forms with water a constant boiling mixture (b.p. 126° to 127°C.) which contains 57% HI. The concentration of hydriodic acid in the reagent used should be not less than 56.5%. The blank determination, which is affected primarily by free iodine in the reagent, should require not more than 0.5 ml. of 0.1 N  $\text{Na}_2\text{S}_2\text{O}_3$ .<sup>6</sup>

**NOTE.**—If necessary, the acid may be purified<sup>7</sup> by adding it to a small amount of red phosphorus and boiling for 20 to 30 min. in a hood while passing a stream of  $\text{CO}_2$  into the liquid. Carry out the distillation behind a safety glass shield in a hood, using an all-glass apparatus with a slow stream of  $\text{CO}_2$  running through the receiver. Under some conditions the poisonous gas phosphine,  $\text{PH}_3$ , is formed during distillation, and this may unite with molecular iodine to form  $\text{PI}_3$  which may explode on contact with air. It is therefore advisable to keep the current of  $\text{CO}_2$  going after the distillation is ended and until the apparatus has cooled; this will prevent air from being sucked into the apparatus. Put the purified HI in small, brown, glass-stoppered bottles, previously swept out with  $\text{CO}_2$ , and seal the stoppers with molten paraffin. Store in a dark place. To minimize decomposition of HI due to contact with air, run  $\text{CO}_2$  into the bottle while withdrawing portions of the acid for use.

**Carbon Dioxide.**—This may be obtained by the interaction of marble and hydrochloric acid (1:1) in a Kipp generator, or dry ice in a Dewar flask; preferably, from a cylinder of the gas equipped with a suitable needle valve. Nitrogen may be used in place of carbon dioxide.

<sup>5</sup> Size O gelatin capsules, available from Parke-Davis Co., have been found satisfactory for this purpose.

<sup>6</sup> Hydriodic acid available from Merck and Co., under the designation "For Methoxy Determination," has been found satisfactory.

<sup>7</sup> Sampsel, E. P., and McHard, J. A., *Ind. Eng. Chem., Anal. Ed.*, 14, 750, 1942; 20, 368-70, 1948.

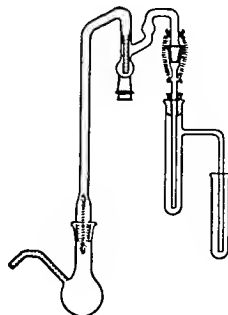


FIG. 38-2. Methoxyl Apparatus.

**Sodium Acetate Solution (200 g per liter)**—Dissolve 220 g of reagent grade anhydrous sodium acetate in water and dilute to 1 liter

**Formic Acid (90%)**

**Potassium Iodide solid KI reagent grade**

**Starch Indicator Solution or Thyodene**

**Standard Sodium Thiosulfate Solution (0.1 N)**—See TAPPI Standard T610m

**Sulfuric Acid 1:10  $H_2SO_4$**

**Test Specimen** Obtain a representative specimen of about 60 mg of air dry wood meal or prepared sawdust having a known moisture content and which has not been in contact with methanol ethanol or other substance. The adsorbed residue of these may amount to as much as 0.5% and will produce a volatile iodide.

**Procedure** Accurately weigh the specimen in a gelatin capsule and place the specimen and capsule in the reaction flask.

Through the condenser add to the trap in the distillation apparatus (Fig. 38.1) enough of the phosphorus slurry to fill the trap about half full. Add 19 to 20 ml of the bromine solution to the receiver.

Add a few small glass beads or chips of clay plate. With a pipet add exactly 2 ml of phenol or preferably propionic anhydride since phenol appears<sup>8</sup> to give slightly low values by 0.3 to 0.5% for woods (but not for lignins)<sup>9</sup>.

Add 6 ml of the hydriodic acid and immediately attach the boiling flask to the condenser using a few drops of HI to moisten the ground glass joint then connect the side of the flask to the feeder and source of carbon dioxide.

Pass the CO<sub>2</sub> into the apparatus at the rate of about 2 bubbles per second. Immerse the flask in the oil bath maintained at a constant temperature at about 150°C and heat for 40 min.

Add 10 ml of the sodium acetate solution to a 500 ml Erlenmeyer flask and wash into it the contents of the receiver dilute to 125 ml with water. Add formic acid dropwise with swirling until the brown color of bromine is discharged and then add about 6 drops more. A total of 12 to 15 drops is usually required. After about 3 min add 3 g of KI and 15 ml of  $H_2SO_4$  (1:10) and titrate immediately with 0.1 N  $Na_2S_2O_3$  to a light straw color. Add the starch indicator and continue the titration to the disappearance of the blue color.

Make a blank methoxyl determination with a gelatin capsule and 2 ml of the propionic anhydride in the reaction flask.

**Calculation**—Calculate the methoxyl in the specimen as follows

$$\text{Percentage methoxyl} = \frac{(A - B)\Lambda \times 0.00517}{W} \times 100$$

where  $A$  = ml of  $Na_2S_2O_3$  solution required for the specimen,

$B$  = ml of  $Na_2S_2O_3$  solution required for the blank,

$\Lambda$  = normality of the  $Na_2S_2O_3$  solution and

$W$  = moisture free weight of the specimen

**Report**—The results as methoxyl in moisture free wood to the nearest 0.01%.

**Additional Information**—This revision is comprehensive and changes the appa

<sup>8</sup> Samsel E. P. private communication

<sup>9</sup> Each milliliter of the propionic anhydride will increase the titration by approximately 0.15 ml of 0.1 N  $Na_2S_2O_3$



ratus and the reagents (HI and phenol) in T 2 m-43. It is adapted from ASTM Method D914-50, Methods of Testing Ethyl Cellulose.

An additive (phenol or propionic anhydride) is necessary because wood meal does not completely disintegrate in boiling hydriodic acid.

### MOISTURE IN WOOD CHIPS AND SAWDUST BY TOLUENE METHOD <sup>10,11</sup>

The following method is generally superior to oven drying and usually gives slightly higher results since cellulose can be completely dried only with difficulty, and then must be weighed in a dry atmosphere. Other volatile impurities, such as turpentine, are not included in the results unless they are soluble in water. It is hence especially valuable for wood chips or sawdust. If only a small sample is available, it is preferable to use the smaller apparatus described in TAPPI Standard T 484 m-58, for paper and paperboard. This method is standardized as TAPPI T 3 m-60.

**Apparatus.** Distillation Apparatus (Fig. 38-3).—The apparatus consists of a glass flask connected to a trap with a reflex condenser discharging into it, means for heating the flask, means for measuring the quantity of a moisture distilled over with the toluene vapor, and a provision for returning the condensed toluene liquid to the flask.

The glass flask is of the short-neck, round-bottom type having a capacity of about two liters.

The moisture trap follows the general plan of that used in the Dean-Stark water determination apparatus but with certain modifications. It is considerably larger than usual and should hold about 100 ml., the exact size not being important. The lower portion is of smaller diameter than the upper part and is graduated in 0.1-ml. divisions. A glass stopcock is sealed on at the bottom to permit drawing off the water for measurement.

The vapor conveying tube between the glass flask should be lagged with insulation such as asbestos tape, subsequently lacquered or shellacked. Although thin, this insulation greatly reduces condensation of the distilling liquid in the vapor tube, thus requiring a lower bath temperature to produce the required refluxing.

The condenser should have a jacket length of at least 24 in. and be closed at its upper end with a standard buret cap or a small test tube, but preferably with a drying tube containing a desiccant, such as indicating anhydrous silica, to prevent interior condensation of atmospheric moisture. Its lower end should be ground off at an angle of 30° to 45°. When inserted in the trap, the tip should extend to about 7 mm. ( $\frac{3}{4}$  in.) above the surface of the liquid in the trap when full. Accurate centering of the tip practically eliminates the collection of droplets of water on the sides of the trap.

Before use, thoroughly clean the condenser and the trap with soap and warm water, rinse well, then treat with hot cleaning solution (a mixture of 10 ml. of saturated potassium bichromate solution and 990 ml. of concentrated sulfuric acid), finally thoroughly rinse and dry.

The heater is preferably an electric heating mantle to fit the flask, although an

<sup>10</sup> U. S. Forest Products Laboratory Bulletin, Chemical Analysis of Pulp and Pulp Woods, Method No. 13, Aug., 1928.

<sup>11</sup> Schwalbe, Z. für Angew. Chem., 21, 408, 1908.

oil bath or an electric heater (as shown in Fig 38 3) or, least desirable of all, a Bunsen burner may be used. If an oil bath is used, the level of the oil should be above that of the liquid in the boiling flask, to reduce bumping.<sup>12</sup>

**Iron Support Stand**, with clamps for the distillation apparatus

**Graduated Cylinders**, 25, 50 or 100-ml capacity or a buret, accurately calibrated to measure the volumes of water having a little toluene layer floating on it

**Containers**, for specimens preferably cans having plug tops or tight fitting lids. Mark each can and its top with a distinguishing number and weigh both together to the nearest 0.5 g

**Balance**, with a capacity of about 1 kg and a sensitivity of at least 0.1 g

**Reagent Toluene**, industrial grade (b.p. 110° to 112°C). This normally contains a little moisture which must be removed before use. To do this, add a few ml of water to about 1 liter of the toluene and distill in the moisture apparatus until no additional water collects in the trap

**NOTES**—The toluene may be used over again until it contains an excess of soluble substances extracted from the wood. Then redistill and retain the portion boiling within the specified range

The amount of toluene required for each determination is about 500 ml. It need not cover the specimen

**Calibration.**—Add a small quantity of toluene to the trap, graduated cylinder or buret used to measure the distillate before calibrating them, since the presence of the toluene will affect the shape of the meniscus formed at the interface. Calibrate by adding known volumes of pure water from a buret which has been previously calibrated. (See TAPPI Standard T 609 m)

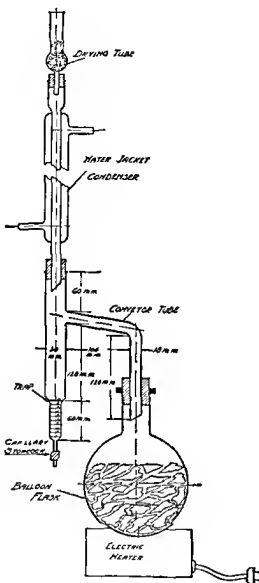


FIG 38 3 Distillation Apparatus

**Test Specimen**—Take a representative specimen of the wood chips or sawdust, place in the tared container and close it quickly to prevent any change in weight due to exposure

<sup>12</sup> For small specimens containing less than 10 g of moisture an alternative and better apparatus having ground glass joints in place of cork stoppers is described in TAPPI Standard T 484 m

The size of the specimen should be such as to yield enough moisture for an accurate measurement, but should not exceed 300 g.

If it is necessary to take a larger quantity in order to get a representative specimen, divide it into smaller portions and test each separately, combining the results. Alternatively, use a 5-l. flask and 1 or 2 liters of toluene.

*Procedure.*—Thoroughly clean the condenser tube and trap, and dry by heating them in an oven at 105°C. While the glass is still warm, wet the inner surfaces of the condenser and the trap with a small quantity of toluene—preferably containing a trace of a silicone—to lessen the probability of water globules sticking to the glass surface. The wetting can be done conveniently by temporarily assembling the apparatus without the drier tube and pouring 15 to 20 ml. of the toluene into it through the condenser tube.

Introduce 500 to 750 ml. of toluene into the flask and add a few glass beads or oven-dried pieces of porous plate to avoid bumping. As rapidly as possible, transfer the weighed specimen from its container to the flask. It is desirable, but not essential, to cover the specimen with the solvent.

Reconnect the apparatus and start the stream of cooling water through the condenser. Apply heat to the flask and regulate it so that the condenser tube immediately below the water jacket is just barely hot. Distill at the rate of about 3 drops per sec. until practically no water is visible on any part of the apparatus except in the bottom of the trap. This usually requires about 1 hr. Then increase the rate of distillation slightly to remove traces of moisture in the condenser tube and wait until the water level in the trap remains unchanged after at least a 10-min. interval.

*NOTE.*—If drops of water adhere to the side of the trap or condenser tube, they usually may be dislodged by rubbing with a copper wire having one end wound into a spiral slightly smaller than the inside of the trap. When drops are observed, the end of the wire may be passed down through the top of the condenser tube without interrupting the distillation. The presence of such drops indicates dirty equipment, so another test should be made if a high degree of accuracy is desired.

Read the volume of water in the trap (without disconnecting the apparatus) to the nearest 0.02 ml. Correct the observation, if necessary, for any error in graduation. It is not necessary to wait until the distillate clears before making the reading.

If the water is above the graduated portion of the trap, either during the distillation or at the end, draw off the water through the stopcock into a small tared beaker and weigh, or into an appropriate size of graduated cylinder or buret, and cool and measure its volume.

*Report.*—Report as the percentage of moisture, distillation method, the total distillate calculated to the nearest 0.1% based on the original (moist) weight of the specimen.

*Precision.*—The method is accurate to within about 0.2 ml. of water. The accuracy of the reported percentage depends on the size of the sample and its moisture content. For a small volume of water that need not be transferred, and with accurate calibration of the trap with water under toluene, the accuracy may be increased to be within 0.1 ml.

**Report.**—Report the soluble matter to the nearest 0.1% based on the moisture-free wood.

**Precision.**—The results of duplicate tests should not vary by more than 5% of the average result. With care, it is possible to keep the deviation below 2%.

**Additional Information.**—The results with this method are usually somewhat higher than those obtained by the older methods in which the temperature of the material during treatment was often below 90°C.

### ETHER SOLUBILITY OF WOOD<sup>14</sup>

The ether-soluble content of wood is a measure of such substances as waxes, fats, resins, phytosterols and non-volatile hydrocarbons. This amount is markedly influenced by seasoning or drying of the wood. This method is standardized as ASTM D1108 and TAPPI T 5 m-59.

**Apparatus.** Filtering Crucibles.—Alundum, porosity R.A. 98., or fritted glass, medium porosity.

**Extraction Apparatus.**—With ground-glass joints. A compact form of Soxhlet apparatus is preferable, consisting of (a) Soxhlet extraction flask of 250-ml. capacity; (b) Soxhlet extraction tube, inside diameter 50 mm., capacity to top of siphon about 100 ml., height of siphon tube about 55 mm. (This type is specified because siphoning is more rapid than extractors with higher siphon tubes. Obtainable from the Scientific Glass Apparatus Company, Bloomfield, N. J.); (c) Hopkins inner-cooled condenser.

**Test Sample.**—In accordance with TAPPI Standard T 11 m (p. 1734), prepare a representative sample of 40/60 mesh (0.25 to 0.40 mm. diameter) air-dried sawdust and determine its moisture content. At least 4 g. are required for a determination in duplicate.

**Procedure.**—Clean, then dry and weigh the Soxhlet extraction flask to the nearest milligram. From the air-dry sample weigh in a tared filtering crucible to the nearest 5 mg. a specimen which is the equivalent of  $2 \pm 0.1$  g. of moisture-free wood. Place the crucible and specimen in position in the Soxhlet apparatus and place a small cone of fine-mesh screen wire in the top of the crucible to prevent any loss of the specimen. Assemble the apparatus, and extract with 200 ml. of U.S.P. ethyl ether for 6 to 8 hours, keeping the ether boiling briskly.

Evaporate the ether from the extraction flask, dry the flask and ether extract in an oven for 1 hour at  $105 \pm 3^\circ\text{C}.$ , cool in a desiccator, and weigh. Continue the drying until there is no further loss in weight. Calculate the weight of the dried residue as a percentage of the moisture-free sawdust.

**Report.**—Report the ether-soluble matter to the nearest 0.1%, based on the moisture-free wood.

### ALCOHOL-BENZENE SOLUBILITY OF WOOD<sup>15</sup>

The alcohol-benzene soluble content of wood is a measure of the waxes, fats, resins, and certain other ether-insoluble components, including possibly portions

<sup>14</sup> Wise, Louis E., and Jahn, Edwin C., *Wood Chemistry*, 2nd ed., esp. Vol. I, Part 3, Reinhold, New York, 1952.

<sup>15</sup> Wise, Louis E., and Jahn, Edwin C., *Wood Chemistry*, 2nd ed., esp. Vol. I, Part 3, Reinhold, New York, 1952.

of some of the so called wood gums and other water soluble components This method is standardized as ASTM D1107 and TAPPI T 6 m 59

**Apparatus** Filtering Crucibles—Alundum porosity R A 98 or glass extraction thimbles with coarse or extra coarse porosity fritted disks

**Extraction Apparatus**—With ground glass joints A compact form of Soxhlet apparatus is preferable consisting of (a) Soxhlet extraction flask of 250 ml capacity (b) Soxhlet extraction tube inside diameter 50 mm capacity to top of siphon about 100 ml height of siphon tube about 55 mm (This tube is specified because siphoning is more rapid than extractors with higher siphon tubes Obtainable from the Scientific Glass Apparatus Co Bloomfield N J) (c) Hopkins inner cooled condenser

**Solvent** Alcohol Benzene Mixture—Mix together 1 volume of approximately 95% ethyl alcohol and 2 volumes of benzene

**Test Sample**—In accordance with TAPPI Standard T 11 m (p 1734) prepare a representative sample of 40/60 mesh (0.25 to 0.40 mm diameter) air dried sawdust and determine its moisture content About 4 g are required for a determination in duplicate

**Procedure**—Clean then dry and weigh the Soxhlet extraction flask to the nearest milligram From the air dry sample weigh to the nearest 5 mg in a tared filtering crucible a specimen equivalent to  $2 \pm 0.1$  g of moisture free wood Place the crucible and specimen in position in the Soxhlet apparatus and place a small cone of fine mesh screen wire in the top of the crucible to prevent any loss of the specimen Extract with 200 ml of alcohol benzene mixture for 6 to 8 hours keeping the liquid boiling briskly

Evaporate the solvent from the extraction flask dry the flask and contents in an oven for 1 hour at  $105 \pm 3^\circ\text{C}$  cool in a desiccator and weigh Continue the drying until there is no further loss in weight Calculate the weight of dried extract as a percentage of the moisture free sawdust

**Report**—Report the alcohol benzene soluble matter to the nearest 0.1% based on the moisture free wood

## HOLOCELLULOSE IN WOOD<sup>16 17</sup>

Holocellulose is the lignin free fibrous material comprising all of the hemicellulose and cellulose in wood It is white cream or straw colored depending upon the kind of wood The Cross and Bevan cellulose does not contain the entire hemicellulose fraction as some is extracted with the lignin This method is standardized as TAPPI T 9 m 54

**Apparatus** Glass Crucibles—With fritted glass bottom Pyrex C or M porosity contained in weighing bottles

**Weighing Bottles**—Of suitable size to contain the glass crucibles

**Chlorination Apparatus**—As shown in Fig 38.4

**Reagents** Alcohol Monoethanolamine Solution—A 3.0% solution (by volume) of monoethanolamine in 95% ethyl alcohol

**Ethyl Alcohol, 95% by volume**

**Test Specimen**—The test specimen shall consist of at least 6 g of air dry extract

<sup>16</sup> Van Beckum W G and Ritter G J Paper Trade J 105, 127-30 Oct 28 193  
Tech Assoc Papers 21, 431-31 June 1938

<sup>17</sup> Kurth E I Paper Trade J 126, 56-58 Feb 5 1948 Tech Assoc Papers 31 611-11 June 1948

tive-free sawdust, prepared according to TAPPI Standard T 12 m (p. 1736), that has previously been ground to pass a 40-mesh sieve and to be retained on a 60-mesh sieve.

**Procedure.**—Weigh accurately in duplicate approximately 2 g. of the prepared sawdust in a tared glass crucible contained in a weighing bottle. Determine the moisture content on the remainder of the test specimen.

Using slight suction, chlorinate the moist sample by passing chlorine gas through a funnel inverted over the crucible, which is in position on a suction flask. Keep the crucible and contents cool with ice water. After chlorinating for 3 minutes, remove the inverted funnel, stir the wood thoroughly, and rechlorinate for 2 minutes.

Add alcohol to dissolve excess chlorine and HCl, and after 1 minute remove by suction. Release the vacuum, drain off the ice water, add sufficient hot alcohol-monoethanolamine (75°C. or higher) to cover the wood completely, and stir thoroughly. Let the solution stand 2 minutes, then remove by suction. Repeat the solvent treatment. Remove any remaining solvent by washing twice with 95% alcohol, then twice with cold water. Remove the wash liquids by suction. The above procedure is not sufficient to remove all the lignin, so repeat the treatment with chlorine and subsequent extraction and washing as outlined above until the color of the residue is white or fails to change with additional chlorination. The second and following treatments with chlorine (after washing the specimen in the crucible with distilled water) should not require more than 2 or 3 minutes. Prolonged action of chlorine gas, together with the HCl formed in the secondary reactions, hydrolyzes the holocellulose and gives low yields. After all the lignin has been removed, wash the fibers twice with alcohol to remove the alcohol-ethanolamine, twice with cold water, and again with alcohol until the residue is neutral to litmus. Finally wash thoroughly with ether to remove all the alcohol and to facilitate drying.

Air-dry the holocellulose to remove excess ether and then dry for 2 and one-half hours at  $105 \pm 3^\circ\text{C}$ . in an oven. (If subsequent analyses or tests are to be made on the holocellulose, it should be dried at  $60^\circ\text{C}$ . in *vacuo*.) Finally place the tared crucible in the original stoppered weighing bottle, cool in a desiccator over concentrated  $\text{H}_2\text{SO}_4$ , and weigh to obtain the holocellulose.

**Report.**—The result shall be reported as percentage by weight of holocellulose in the moisture-free, unextracted wood to one decimal place.

**Additional Information.**—1. A fraction comparable to Cross and Bevan cellulose can be determined from the holocellulose as follows:

Place the crucible and contents from the holocellulose determination (dried in *vacuo* at  $60^\circ\text{C}$ .) in a 600-ml. beaker and add 200 ml. of boiling 1.3%  $\text{H}_2\text{SO}_4$ . Place the beaker and contents in a boiling water bath having a liquid level coinciding with that of the solution in the beaker and continue hydrolysis for 2 hours. Maintain the original levels of the acid solution and the water bath by the addition of water.

Remove the crucible from the acid and wash back into the beaker with distilled

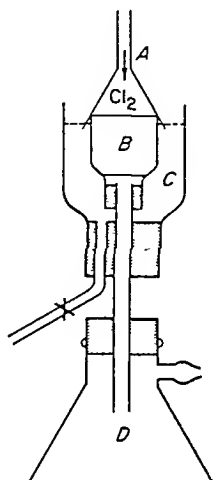


FIG. 38-4. Chlorinator for Holocellulose: A, Glass Funnel; B, Pyrex Fritted-Glass Filtering Crucible; C, Cold Water; D, Suction Flask.

water any of the suspension remaining on its outer surface. Filter the acid mixture through the same crucible and wash the hydrolyzed holocellulose residue with hot water under suction until neutral to litmus then with 20 ml of alcohol and finally with 20 ml of ether. Air dry the residue to remove the excess ether and then dry to constant weight in an oven at  $105 \pm 3^\circ \text{C}$ . Calculate the weight as the percent age of Cross and Bevan cellulose on the basis of the moisture free specimen.

2 The lignin content determined by the sulfuric acid method plus the holocellulose content of the moisture free wood should theoretically equal 100%.

### SAMPLING AND PREPARING WOOD FOR ANALYSIS<sup>18</sup>

**Sampling**—The following procedures are applicable to the preparation of wood samples for all chemical tests. This method is standardized as TAPPI T 11 m-59.

Select samples for chemical analysis in such a way that they are representative of the entire shipment.

**Logs**—Select a typical log from each of not less than 5% of the total number of units to be represented i.e. carloads truckloads cords etc. but not less than 5 logs to make up the aggregate for which the sample is to be representative unless the total number of logs to be sampled is less than five.

Obtain a composite sample of wood from the selected logs by either of the following procedures:

1 Use a power-driven sharp saw having a guide to permit cuts being made across the end of each log just the width of the saw teeth the saw being fitted with a clean box or other device for collecting all the sawdust without contaminating the sample. With the guide removed from the saw cut about one third of the length off one or both ends of each sample log across a portion free from knots or decayed wood.

**NOTE** If the shipment is to be analyzed for its quantity of decay for example by TAPPI Standard T 4 m (p. 1730) take special care in selecting the sample logs take double the number specified above and take cuts across five cross sections of each log at intervals of one sixth of its length.

Remove any bark from the sawed ends of the logs. Replace the guide completely clean the box or collecting device then take one or more cuts across each of the sawed ends of all the logs and collect all the sawdust.

2 Saw a sample disk  $\frac{1}{4}$  to 1 in. thick from each log taking the disk from a point not nearer the end than one third the total length of the log. If only a single log is provided for analysis saw three such disks from it one from approximately the center of the log and the other two about 6 in. from the ends. Cut all the disks into two semicircles or into four sectors by two cuts at an angle depending upon the amount of sample required. Include opposite equal sectors in the final sample. Separate and discard all bark and knots and unless required specifically decayed portions compression wood and other abnormalities. Reduce equal sectors situated opposite in the log from each semicircle to sawdust by means of the specially equipped power-driven saw described above using the portion to be discarded for feeding the selected sector to the saw. Alternatively a hand rasp may be used to produce a satisfactorily divided sample from the sectors if care is taken to keep the teeth of the rasp clear and not to heat the wood unduly by vigorous rasping.

<sup>18</sup> Wise, Louis E. and Jahn, Edwin C. *Wood Chemistry* 2nd ed. esp. Vol. II pp. 1190-20. Reinhold, New York, 1952.

In each case reduce a complete sector to sawdust or raspings so as to ensure the correct proportion of sapwood and heartwood.

**Chips or Sawdust.**—If the sample is in the form of chips, sawdust, or otherwise subdivided wood, secure a number of representative portions to ensure a fair analysis of the lot. If necessary, reduce the amount of material for analysis by quartering in the manner prescribed for coal.

**Grinding and Screening.**—If moist, let the composite sample air-dry thoroughly. Separate the finer material by sifting on a 40-mesh screen, and grind the coarser material in a mill of the Wiley type. A hand-driven grinding mill may also be found suitable. In no case, however, should a mill be used which heats the material appreciably during grinding or which produces an undue proportion of fines. It is preferable to use a power-driven screen because then the fine material may be more effectively separated. Again separate the finer material by sifting, re-grinding any which is retained on the 40-mesh screen; and continue this procedure until all the sample passes through the screen. Sift the material after each passage through the grinding mill before re-grinding, so as to minimize the amount of fines produced.

Place the entire sample so prepared in an air-tight container, e.g., a Mason jar, from which portions may be withdrawn for analysis as desired. It is well to expose the prepared sample to average atmospheric conditions for a period before closure, to minimize changes in the moisture content of the material during subsequent handling and weighing operations.

**Moisture Content.**—If the percentage of moisture-free wood in the sample is required, proceed as follows:

Weigh a specimen of approximately 2 g. into a tared weighing bottle, preferably of the shallow type. Dry for 2 hr. in an oven at  $105 \pm 3^{\circ}\text{C.}$ , cool in a desiccator, open the stopper momentarily to let in the air, and weigh. Continue heating for successive hourly periods until the weight is constant. Calculate and record the percentage of moisture-free wood in the enclosed sample.

**Additional Information.**—The particle size to which wood should be reduced for the purpose of certain analyses has been the subject of differences of opinion. There are two viewpoints:

(a) All the wood sample should be ground to pass a 40-mesh screen, and no further fractionation of the fine material should be permitted. Particles of 40-mesh (0.4 mm. diameter) and smaller are readily attacked by the reagents used in present analytical methods (except the cellulose method), and finer grinding may degrade the wood. Furthermore, for certain analyses, the fine material should not be discarded, because fractionation of the wood meal may alter the proportion of some constituents, for example, decay, and lead to erroneous results.

(b) Wood samples should be of fairly uniform particle size. Especially in the determination of the cellulose content is this desirable to avoid overtreatment of the smaller particles before the larger are completely delignified. Various ranges of particle size have been chosen for the sample for this determination, the one now most favored being that passing a 40- and retained on a 60-mesh screen (40/60 mesh material = from 0.25 to 0.40 mm. diameter).

Unless specified in a particular method, state the range of particle sizes employed for the analysis of the wood as a part of the report.



LIGNIN IN WOOD<sup>19, 20, 21</sup>

When wood is treated with strong acids, the carbohydrates are hydrolyzed, leaving an insoluble residue which is determined as lignin. Since some of the wood extractives would remain insoluble with the lignin, these are first removed by proper solvents. The 72% sulfuric acid method for lignin contains two and sometimes three preliminary extractive treatments, namely: (1) with alcohol, to remove the catechol tannins; (2) with alcohol-benzene solution, to remove the resins, oils, fats, and waxes; and (3) with hot water, to remove the remaining water-soluble materials.

The alcohol extraction is necessary in analysis of woods high in tannin, e.g., oak, chestnut, redwood, etc. It has not been shown necessary in the more common pulpwoods, such as the various species of spruce, pine, fir, hemlock, poplar, birch, beech, and maple. It is recommended that for these woods the alcohol extraction be omitted unless it is desirable for a special purpose. In analysis of woods not listed, the desirability of the alcohol extraction depends upon the purpose of the analysis, and the report should state whether or not alcohol extraction was used. This method is standardized as TAPPI T 13 m-54.

**Apparatus.** Filtering Crucibles.—Alundum, porous porcelain, or fritted-glass crucibles (all of fine porosity), or Gooch crucibles with an acid-washed asbestos mat, are recommended for filtering the separated lignin. (Glass crucibles cannot be used if the lignin is to be ashed.)

**Extraction Apparatus.**—A Soxhlet apparatus is preferable, consisting of (a) Soxhlet extraction flask, 250-ml. capacity; (b) Soxhlet extraction tube, inside diameter 45 to 50 mm., capacity to top of siphon approximately 100 ml.; (c) condenser; (d) extraction crucibles of alundum or fritted glass and of medium or fine porosity. The extraction tubes specified siphon more rapidly than extractors with higher siphon tubes.

**Reagents.** Alcohol-Benzene Solution.—Mix 33 volumes of approximately 95% ethyl alcohol and 67 volumes of c.p. benzene.

**Sulfuric Acid, 72%.**—Carefully pour 665 ml. of concentrated  $\text{H}_2\text{SO}_4$  into about 300 ml. of water and, after cooling, dilute to 1 liter. Standardize against standard sodium hydroxide solution, using methyl orange indicator. Adjust the acid to a strength of  $72 \pm 0.1\%$ , by addition of water or concentrated  $\text{H}_2\text{SO}_4$ , as may be found necessary.

**NOTE.**—As concentrated  $\text{H}_2\text{SO}_4$  varies somewhat in strength, the measurement does not have to be made accurately; it may be done with a liter graduate. The proportions given are for concentrated  $\text{H}_2\text{SO}_4$  of 96% strength and 1.84 sp. gr.

If desired, the solution may be standardized by an accurate determination of its specific gravity. For 72%  $\text{H}_2\text{SO}_4$  the specific gravity at  $20^\circ/4^\circ\text{C}$ . is 1.6338; and at  $60^\circ/60^\circ\text{F}$ . or  $15.56^\circ/15.56^\circ\text{C}$ . it is 1.6389. A variation of 0.1% in the strength of the acid at this concentration causes a change of 0.0012 in the specific gravity.

**Test Specimen.**—The test specimen shall consist of sawdust that has previously been ground to pass a 40-mesh sieve, and thoroughly air-dried. (See TAPPI Standard T 11 m, p. 1734.)

<sup>19</sup> Bray, M. W., Paper Trade J., 87, No. 25:29, Dec. 20, 1928.

<sup>20</sup> Ritter, G. J., Seborg, R. M., and Mitchell, R. L., Ind. Eng. Chem., Anal. Ed., 4, 202, 1932.

<sup>21</sup> Ritter, G. J., and Barbour, J. H., Ind. Eng. Chem., Anal. Ed., 7, 238, 1935.

**Apparatus.** Crucible.—A platinum crucible or dish with lid or cover is recommended. If platinum is not available, silica may be used.

**Analytical Balance.**—Having a sensitivity of 0.1 mg. and with class S weights.

**Electric Muffle Furnace.**—Adjusted to maintain a temperature of  $575 \pm 25^{\circ}\text{C}$ .

**Test Specimen.**—Obtain a representative sample of the wood, prepared, for example, in accordance with T 11 m (p. 1734). Weigh to 5 mg. or less a specimen of about 5 g. of moisture-free wood for ashing, preferably in duplicate. If the moisture in the sample is not known, determine it by drying a corresponding specimen to constant weight at  $105 \pm 3^{\circ}\text{C}$ .

**Procedure.**—Carefully clean the empty crucible and cover, and ignite to constant weight in a muffle furnace at  $575 \pm 25^{\circ}\text{C}$ . After ignition, cool slightly and place in a desiccator, preferably containing indicating-grade anhydrous alumina. When cooled to room temperature, weigh the ignited crucible on the analytical balance to the nearest 0.1 mg.

Place all, or as much as practicable, of the weighed specimen in the crucible. If the crucible is large enough, the entire specimen may be weighed in it. Burn the wood directly over a low flame of a Bunsen burner (or preferably on the hearth of the furnace), until it is well carbonized. If the crucible is too small to hold the entire specimen, gently burn the portion added and add more as the flame subsides. Take care not to blow portions of the ash from the crucible. Continue heating with the burner only as long as the residue burns with a flame. When the flame has died down, place the crucible in the furnace at  $575 \pm 25^{\circ}\text{C}$ . for a period of at least 3 hours, or longer if needed to burn off all the carbon.

When ignition is complete, as indicated by the absence of black particles, remove the crucible from the furnace, replace the cover, and allow to cool somewhat. Then place in a desiccator and cool to room temperature. Reweigh with the ash to the nearest 0.1 mg. and calculate the percentage based on the moisture-free weight of the wood.

**Report.**—Report the ash as a percentage of the moisture-free wood to two significant figures, or to only one figure if the ash is less than 0.1%.

**Precision.**—The results of duplicate determinations should be suspect if they differ by more than 0.5 mg.

**Additional Information.**—Since the ignition temperature affects the weight of the ash, only values obtained at  $575 \pm 25^{\circ}\text{C}$ . should be reported as being in accordance with this standard.

In this revision, the temperature of ignition has been specified at  $575 \pm 25^{\circ}\text{C}$ . in place of  $600^{\circ}\text{C}$ ., being the same as in Ash in Pulp (p. 1766).

## CELLULOSE IN WOOD<sup>22, 23</sup>

The procedure here described isolates the total cellulose in wood by a process of chlorination. The cellulose thus obtained is sometimes referred to as Cross and Bevan cellulose. As the method is empirical, details must be carefully followed. This method is standardized as TAPPI T 17 m-46.

**Apparatus.** Chlorination Apparatus.—A special chlorination apparatus as illustrated in Fig. 38-5 is required for this determination. It consists of one leveling tube and holder, two individual glass three-way stopcocks, one thermometer, one

<sup>22</sup> Bray, M. W., and Andrews, T. M., Paper Trade J., 76, 47, Feb. 22, 1923.

<sup>23</sup> U. S. Forest Products Laboratory, Standard Testing Manual for Pulpwood, Pulp, Stuff, and Paper.

Hempel precision gas buret fitted with a three way stopcock, a glass water jacket for the gas buret and a Hempel gas pipet

Glass Crucibles.—Of about 40 ml capacity equipped with a fritted-glass bottom of medium porosity (Pyrex M, or equivalent)

Alundum Crucibles.—Of about 40 ml capacity and of porosity RA 98

Reagents Alcohol Benzene—A mixture of 33 volumes of approximately 95% ethyl alcohol and 67 volumes of c.p. benzene

Calcium Chloride Solution for Gas Buret and Gas Pipet.—Saturate water with  $\text{CaCl}_2$  at room temperature bubble chlorine gas in until saturated, and filter to

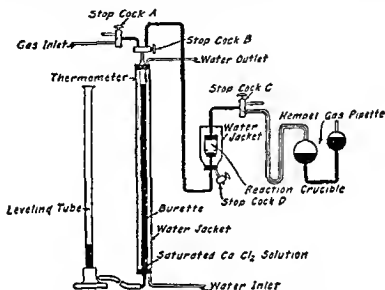


FIG. 38.5 Apparatus for Cellulose Determination

use. When the apparatus is not in use it is well to have it filled with fresh  $\text{Cl}_2$  gas, thus keeping the  $\text{CaCl}_2$  solution saturated.

Chlorine.—In a tank or cylinder under pressure

Sulfur Dioxide Solution.—Approximately 3%. Pass a stream of  $\text{SO}_2$  gas into 100 ml of distilled water at about  $25^\circ\text{C}$  ( $77^\circ\text{F}$ ) until saturated. Then dilute with 200 ml of distilled water at the same temperature. (This should give approximately a 3.1% solution if prepared at  $25^\circ\text{C}$ , 2.6% at  $30^\circ\text{C}$ , and 3.8% at  $20^\circ\text{C}$ ). The exact strength is not important but since there is a tendency toward loss of strength due to possible incomplete saturation, it is preferable not to have the temperature much above  $25^\circ\text{C}$ .)

Sodium Sulfite Solution, 2%.—Dissolve 20 g of anhydrous  $\text{Na}_2\text{SO}_3$  or 40 g of  $\text{Na}_2\text{SO}_3 \cdot 7\text{H}_2\text{O}$  in distilled water and dilute to 1 liter.

Test Specimen.—The specimen shall consist of about 2 g of a representative sample of air-dry disintegrated wood of known moisture content.

The samples of wood for analysis shall be prepared according to the procedure described on p. 1734.

Procedure.—Weigh accurately approximately 2 g of the prepared air-dry wood in a tared alundum crucible contained in a weighing bottle. Extract the crucible

with contents for 6 hours, or overnight if more convenient, in a Soxhlet extractor with alcohol-benzene mixture. After evaporation of the solvent, wash the sawdust thoroughly with hot water, using a suction pump. Then transfer the moist material to a glass crucible with fritted-glass bottom. The crucible is water jacketed and connected between the gas buret and the gas pipet, as shown in Fig. 38-5, by means of two rubber stoppers through which passes a capillary glass tubing. Apply suction, first at the bottom of the crucible until the excess moisture is removed, and then at the top. This removes the water from the fritted-glass plate and evenly distributes the remaining moisture throughout the entire sample.

Pass a buret-full of Cl gas from the buret up through the material in the crucible and over into the gas pipet as fast as possible. The temperature of the water in the water jacket should be between 23.5 and 32°C. (74 and 90°F.). During the first chlorination, samples of wood absorb approximately 230 ml. of Cl gas at room temperature and atmospheric pressure. This necessitates refilling the buret, which may be done quickly as it is connected to a Cl tank with a three-way stopcock. The first chlorination treatment requires from 3 to 4 minutes, after which remove the crucible from the apparatus and wash the material by suction with approximately 50 ml. of distilled water, and successively with 50 ml. of approximately 3%  $\text{SO}_2$  solution, 50 ml. of water, then 50 ml. of freshly prepared 2%  $\text{Na}_2\text{SO}_3$  solution. Transfer the material to a 250-ml. Pyrex beaker, using a pointed glass rod, the last traces of material being removed from the crucible with 100 ml. of 2%  $\text{Na}_2\text{SO}_3$  solution in the following manner:

Add approximately 15-ml. portions of the  $\text{Na}_2\text{SO}_3$  solution to the crucible for each rinsing. When 60 ml. have been thus used, place 10-ml. portions of the remaining 40 ml. in a watch glass, and by means of gentle suction applied to the top of the crucible, placed on the watch glass, remove all of the material from the fritted-glass bottom of the crucible. A rubber policeman drawn gently over the bottom of the crucible assists in removing the last traces.

Cover the beaker containing the sample with a watch glass and place in a boiling-water bath for 30 minutes. Again transfer the fibers to the glass crucible and wash with about 250 ml. of distilled water.

The above procedure is never sufficient to remove all the lignin, so that the treatment with Cl and subsequent washing with  $\text{SO}_2$  solution, water, and  $\text{Na}_2\text{SO}_3$  solution as outlined above must be repeated until the fibers show only a very faint tinge of pink upon addition of the  $\text{Na}_2\text{SO}_3$  solution. The second and following treatments with Cl (after washing the specimen in the crucible with distilled water) should not require more than 2 or 3 minutes. Prolonged action of Cl gas, together with the HCl formed in the secondary reactions, hydrolyzes the cellulose, gives low yields, and causes varying amounts of alpha-cellulose.

After all the lignin has been removed, transfer the fibers to the alundum crucible and wash thoroughly by suction successively with 500 ml. of hot water, 50 ml. of 95% alcohol, and finally with 50 ml. of ether. Then dry for 2 and one-half hours at  $105^\circ \pm 3^\circ\text{C}$ . in an oven.

Finally place the tared alundum crucible in the original stoppered weighing bottle, cool in a desiccator over concentrated  $\text{H}_2\text{SO}_4$  and weigh the residual cellulose.

**Report.**—The weight of the residue shall be calculated, to one decimal place, as a percentage of the moisture-free weight of unextracted wood and reported as cellulose.

## PENTOSANS IN WOOD

Pentosans are a part of the noncellulosic carbohydrates present in wood and consist chiefly of xylan and araban. The latter substances are converted to furfural with strong hydrochloric acid (HCl). In this method the furfural formed by the action of hot HCl on the pentosans in wood is distilled from the mixture in the manner prescribed by the A O A C<sup>24</sup>. The distillates may be analyzed by either a gravimetric or a volumetric procedure. Pentosans in pulp and paper are deter-

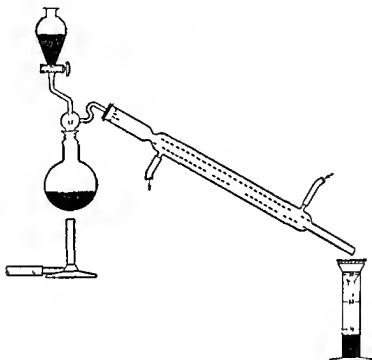


FIG 38 6 Apparatus for the Determination of Pentosans

mined by a volumetric method, but insufficient experimental data exists to ascertain the accuracy of the volumetric method for the determination of pentosans in all kinds of wood. This method is standardized as TAPPI T 19 m 50.

**Apparatus.** Distilling Flask, 300 ml.—This flask is connected to a long water-cooled condenser. A separatory or dropping funnel is mounted in the neck of the distilling flask. Rubber stoppers may be used to make the connections. It is preferable, however, to use a 300 ml round bottom flask with a No. 24/40 glass stopper, as shown in Fig. 38 6.

Graduated Cylinder, 100 ml.—Provided with a funnel for collecting the distillate.

Gooch Crucibles.

**Reagents.** Hydrochloric Acid, 12% (sp. gr. 1.06).—Dilute 307 ml of c.p. concentrated HCl (sp. gr. 1.18 to 1.19) to 1 liter with water.

Phloroglucinol Solution.—Dissolve 11 g of pure phloroglucinol in 300 ml of

<sup>24</sup> Assoc. Off. Agr. Chemists, *Methods of Analysis*, 6th ed., p. 412, 1945.

warm 12% HCl and dilute to 1500 ml. with cold 12% HCl. If diresorcin is present, it will crystallize out after standing for a week. Filter immediately before using.

**Aniline Acetate Reagent.**—Add acetic acid slowly to a mixture containing equal volumes of aniline and water until the liquid becomes clear after shaking.

**Test Specimen.**—The test specimen shall consist of 1.5 g. of air-dry wood meal of known moisture content and so chosen as to represent the entire lot being tested.

**NOTE.**—The weight of the sample should be such that the weight of phloroglucide obtained does not exceed 0.3 gram.

It shall be prepared for analysis in accordance with TAPPI Standard T 11 m (p. 1734). If extractive-free wood meal is used for analysis, it shall be prepared in accordance with T 12 m (p. 1736).

**Procedure.**—Place the accurately weighed sample in the 300-ml. distilling flask, together with a small piece of paraffin to eliminate foaming and a few glass beads or several pieces of recently ignited pumice stone to prevent bumping. Add 100 ml. of 12% HCl, place the flask on a wire gauze, connect with a condenser, heat gently at first with a Bunsen burner, and then regulate so as to distill over 30 ml. in each 10 minutes. More rapid distillation gives low results. Pass the distillate through a small filter paper before it enters the receiver, and keep the tip of the condenser as close as possible to the filter paper.

As soon as 30 ml. of distillate are collected, add another 30-ml. portion of 12% HCl from the separatory funnel in such a manner as to wash down particles adhering to the sides of the flask. Continue the distillation in this manner until 360 ml. of distillate are collected. To the total distillate add gradually with stirring 40 ml. of filtered phloroglucinol solution that has been prepared at least a week previously. The distillate will soon turn greenish black. Allow the solution to stand 16 hours. After this period the amorphous black precipitate of furfural phloroglucide will have settled to the bottom of the beaker. Test the clear supernatant liquid with aniline acetate paper. If a drop of the liquid gives a pink color with aniline acetate paper, the precipitation of the furfural is incomplete, in which case add a further amount of phloroglucinol solution and again allow the mixture to stand 16 hours.

**NOTE.**—The quantity of phloroglucinol used should be about double that needed for complete precipitation.

Collect the furfural phloroglucide in a weighed Gooch crucible having a thick asbestos mat. Wash the precipitate with exactly 150 ml. of cold water in such a way that the water is not entirely removed from the crucible until the washing is completed. Dry the crucible for 2 and one-half hours in an air oven at 100 to 105°C. Cool in a stoppered weighing bottle and weigh. The increase in weight is considered to be furfural phloroglucide.

**Calculation.**—The weight of pentosans corresponding to the weight of furfural phloroglucide is found as follows:

$$\text{Pentosans} = (a + 0.0052) \times f$$

where  $a$  = weight of furfural phloroglucide in grams and

$f$  = 0.895 if  $a$  is less than 0.03 g.

= 0.887 if  $a$  is between 0.03 and 0.3 g.

= 0.882 if  $a$  is more than 0.3 g.

**NOTE**—The factor 0.0052 represents the weight of the phloroglucide that remains dissolved in the 400 ml of acid solution

**Report**—The pentosans calculated from the furfural phloroglucide, shall be reported as a percentage of the weight of the moisture free sample to one decimal place

The results of duplicate determinations shall agree within 0.4

# ANALYSIS OF PULP

## CELLULOSE IN PULP<sup>25, 26, 27, 28</sup>

The procedure here described isolates the total cellulose in pulp by a process of chlorination. The cellulose thus obtained is sometimes referred to as Cross and Bevan cellulose. As the method is empirical, details must be carefully followed. This method is standardized as TAPPI T 201 m-54.

**Apparatus.** Chlorination Apparatus.—A special chlorination apparatus as illustrated in Fig. 38-7 is required for this determination. It consists of one leveling tube and holder, two individual glass three-way stopcocks, one thermometer, one Hempel precision gas buret fitted with a three-way stopcock, a glass water jacket for the gas buret, and a Hempel gas pipet.

**Glass Crucibles of About 40-ml. Capacity.**—Equipped with a fritted-glass bottom of medium porosity (Pyrex M, or equivalent).

**Alundum Crucibles** of about 40-ml. capacity and of porosity R. A. 98.

**Reagents.** Calcium Chloride Solution for Gas Buret and Gas Pipet.—Saturate water with  $\text{CaCl}_2$  at room temperature, bubble chlorine gas in until saturated, and filter for use. When the apparatus is not in use, it is well to have it filled with fresh  $\text{Cl}$  gas, thus keeping the  $\text{CaCl}_2$  solution saturated.

**Chlorine.**—In a tank or cylinder under pressure.

**Sulfur Dioxide Solution, Approximately 3%.**—Pass a stream of  $\text{SO}_2$  gas into 100 ml. of distilled water at about 25°C. (77°F.) until saturated. Then dilute with 200 ml. of distilled water at the same temperature. (This should give approximately a 3.1% solution if prepared at 25°C.; 2.6% at 30°C.; and 3.8% at 20°C. The exact strength is not important, but since there is a tendency toward low strength due to possible incomplete saturation, it is preferable not to have the temperature much above 25°C.)

**Sodium Sulfite Solution, 2%.**—Dissolve 20 g. of anhydrous  $\text{Na}_2\text{SO}_3$  or 40 g. of  $\text{Na}_2\text{SO}_3 \cdot 7\text{H}_2\text{O}$  in distilled water and dilute to 1 liter.

**Test Specimen.**—The specimen shall consist of about 2 g. of a representative sample of air-dry disintegrated pulp of known moisture content. The disintegration may be accomplished by rasping or by tearing apart by hand.

**Procedure.**—Weigh accurately approximately 2 g. of the air-dry pulp in a tared alundum crucible contained in a weighing bottle. Wash thoroughly with hot water, using a suction pump, then transfer the moist material to a glass crucible with fritted-glass bottom. The crucible is water-jacketed and connected between the gas buret and the gas pipet, as shown in Fig. 38-7, by means of two rubber stoppers through which passes a capillary glass tubing. Apply suction, first at the bottom of the crucible until the excess moisture is removed, and then at the top. This

<sup>25</sup> Biay, M. W., and Andrews, T. M., Paper Trade J., 76, 47, Feb. 22, 1923.

<sup>26</sup> Bray, M. W., Paper Trade J., 87, 59, Dec. 20, 1928.

<sup>27</sup> Roe, Ralph B., J. Ind. Eng. Chem., 16, 808, 1924.

<sup>28</sup> U. S. Forest Products Laboratory, Standard Testing Manual for Pulpwood, Pulp, Stuff, and Paper.



tion. The second and following treatments with Cl (after washing the specimen in the crucible with distilled water) should not require more than 2 or 3 minutes. Prolonged action of Cl gas, together with the HCl formed in the secondary reactions, hydrolyzes the cellulose, gives low yields, and causes varying amounts of alpha-cellulose.

After all the lignin has been removed, transfer the fibers to the alundum crucible, and wash thoroughly by suction successively with 500 ml. of hot water, 50 ml. of 95% alcohol, and finally with 50 ml. of ether. Then dry for 2 and one-half hours at  $105 \pm 3^\circ\text{C}$ . in an oven.

Finally place the tared alundum crucible in the original stoppered weighing bottle, cool in a desiccator over concentrated  $\text{H}_2\text{SO}_4$  and weigh the residual cellulose.

Report.—Calculate the weight of the residue, to one decimal place, as a percentage of the moisture-free weight of the pulp and report as cellulose.

### CHLORINE CONSUMPTION OF PULP

This is essentially the Roe chlorination method<sup>29</sup> as modified by Johansson<sup>30</sup> and subsequently by Mitchell.<sup>31</sup> It can be used to indicate the degree of cooking of unbleached sulfite, sulfate, soda, or NSSC pulps. This method is standardized as T 202 os-61.

**Apparatus.** Reaction Apparatus (shown in Fig. 38-8).—The gas buret *A* has a capacity of 120 ml. and is graduated in 0.2-ml. divisions. It is connected by a 2-mm. bore glass capillary tubing through stopcock  $S_2$  to an upper, ungraduated chamber or reservoir *D*, of approximately 60-ml. capacity. Both are water-jacketed by glass tubes fitted with rubber bungs. Chamber *D* is closed by a ground-glass, closed-bottom, standard-taper stopper, and is connected by 2-mm. bore glass tubing and stopcock  $S_3$  to a gas pipet  $C_1C_2$ . Buret *A* is also connected by 2-mm. bore tubing to  $S_1$ , a three-way cock through which dry chlorine gas may be introduced from a cylinder into the buret, or excess chlorine may be discharged to waste. Ground-glass ball-joint fittings are used to connect *A*, *D*, and *C*. Buret *A* is connected at the bottom with stout  $\frac{1}{4}$ -in. bore, neoprene tubing, about 4 ft. long, to a leveling bottle *B*. A calibrated thermometer *T* is suspended from the top rubber bung and is wholly immersed in the water in the jacket. The whole apparatus is appropriately mounted, including a sliding support for the leveling bottle *B*, so arranged that the bottle may be supported at any desired height. Means are also provided to continuously circulate water with a temperature of  $25^\circ\text{C}$ . through the two jackets.

Twin units would permit duplicate determinations to be made only a few minutes apart.

Figure 38-9 shows a second reaction apparatus, which, although no longer standard, is still used.

**Other Apparatus.**—Small Büchner funnel and flask, barometer, exhaust hood.

<sup>29</sup> Roe, Ralph B., Paper Trade J., 79, No. 15, 43-6, Oct. 9, 1924; Ind. Eng. Chem., 16, No. 8, 808-11, 1924.

<sup>30</sup> Johansson, David, Paper Trade J., 101, No. 13, 101-4, Sept. 26, 1935; Tech. Assoc. Papers, 19, 431-4, 1936.

<sup>31</sup> Mitchell, Claude R., A Study of the Roe Chlorine Number, Pulp and Paper Research Institute of Canada, Tech. Report No. 69, Jan. 1958.

**Other Materials**—Compressed air supply (not essential) and Silicone stopcock grease

**NOTE**—One part of Dow Corning High Vacuum Silicone grease and two parts of Vaseline or Kel-F fluorocarbon lubricant may be used for the stopcocks. The greases are readily removed with acetone and should be replaced daily.

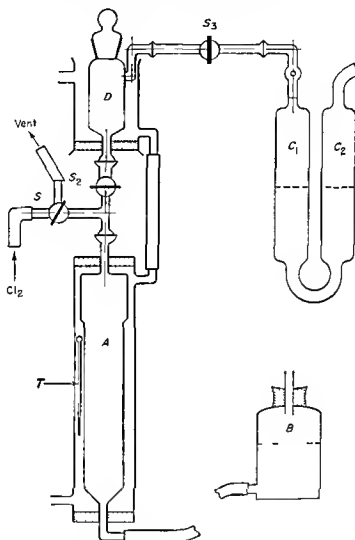


FIG. 38.8 Recommended Reaction Apparatus

**Reagents** Calcium Chloride—Nearly saturated solution of  $\text{CaCl}_2$ . Prepare a saturated solution and add 5% by volume of water.

Chlorine, cylinder of compressed gas

**Test Specimen**—Take a representative sample of at least 4 g of pulp and disintegrate thoroughly if not completely defibered. Acidify with dilute  $\text{HCl}$  to dissolve any carbonates present (e.g.,  $\text{CaCO}_3$ ). With the Buchner funnel and suction flask make a sheet having a dry weight of about 2 g and wash well with distilled water. Make and wash a second sheet and allow both sheets to dry together.

in the vicinity of the balance (preferably under constant temperature and humidity conditions). Determine the percentage of moisture in one of the samples. Weigh, to the nearest milligram, sufficient pulp from the other sheet which, it is estimated, will consume between 30 to 80 ml. of chlorine. (This will vary between 0.4 g. for a high yield chemical pulp to 2.0 g. for well-cooked pulp.)

**Procedure.**—Assemble the apparatus in the exhaust hood with the reaction chamber *D* empty and turn on the 25°C. circulating water. Lubricate the stopper *D*, the balljoints, and the stopcocks with the fluorocarbon grease. Fill the gas buret

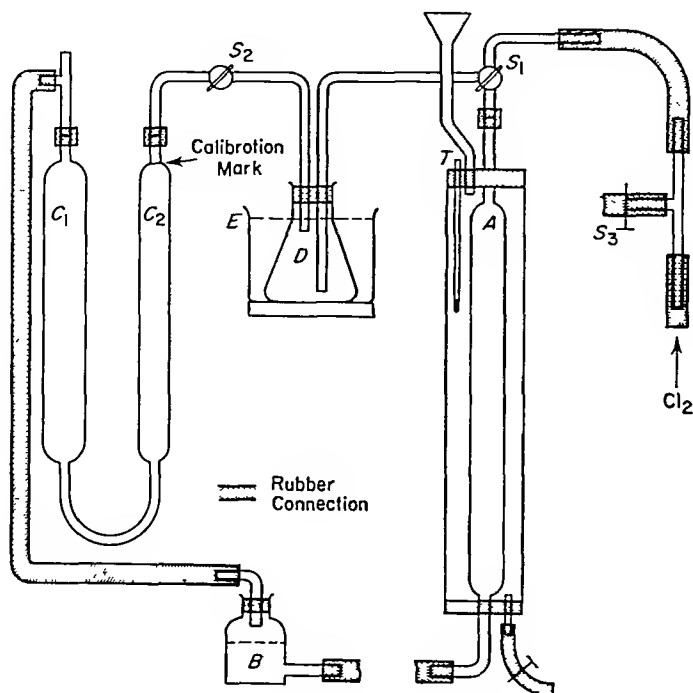


FIG. 38-9. Reaction Apparatus.

*A*, the tubing, and the bottom of leveling bottle *B* with sufficient  $\text{CaCl}_2$  solution so that at least the connecting tubing remains full when the buret *A* is full. Place sufficient  $\text{CaCl}_2$  solution in the gas pipet *C* so that 10 to 20 ml. remains in *C*<sub>2</sub> when *C*<sub>1</sub> and the tubing to *S*<sub>3</sub> are full. Saturate the  $\text{CaCl}_2$  solution in buret *A* and bottle *B* by passing chlorine through *S*<sub>1</sub> (with *S*<sub>2</sub> closed) through *A* and the tubing to *B*, and then to waste through the hood. To saturate the solution in *C*<sub>1</sub>, clamp the tubing between *A* and *B*, place the stopper in vessel *D*, open *S*<sub>3</sub>, and pass chlorine through *S*<sub>1</sub>, *S*<sub>2</sub>, *D*, *S*<sub>3</sub>, *C*<sub>1</sub>, and then *C*<sub>2</sub> to waste through the hood. Make sure that all the balljoints are properly seated, that the apparatus is leakproof, and that the  $\text{CaCl}_2$  solution is completely saturated with chlorine. This is ascertained by running a blank test overnight, using the chlorine but no specimen. There should be no resulting change in the volume of the added chlorine after this operation. The  $\text{CaCl}_2$  solutions need to be freshly saturated with chlorine only at the commencement of a series of successively performed tests, or after a stand-by interval exceeding 1 hr.

Make a blank determination, by exactly the same procedure but, in place of the specimen, use an equivalent amount of quantitative grade filter paper wetted to contain approximately the same percentage of water as the specimen.

Calculate the chlorine number as grams of chlorine consumed in 15 min. at 25°C. by 100 g. of moisture-free pulp, as follows:

$$\text{Chlorine number} = \frac{0.000423(V - b)h}{g(1 + 0.00366t)}$$

where  $V$  = volume of chlorine consumed by the pulp, in milliliters,

$b$  = volume of chlorine consumed in the blank determination, in milliliters,

$t$  = temperature in °C.,

$g$  = grams of moisture-free pulp, and

$h$  = barometric pressure, in millimeters of mercury.

**Report.**—Report the Chlorine Number as grams of chlorine consumed per 100 g. of moisture-free pulp, to the nearest 0.1%.

**Precision.**—Duplicate tests on a single pulp sample are expected to agree 95% of the time, within 5% of each other.

### ALPHA-, BETA-, AND GAMMA-CELLULOSE IN PULP<sup>32, 33</sup>

Cellulose pulp consists of two arbitrarily defined main carbohydrate fractions: the alpha-fraction of high molecular weight, which remains when a mixture of pulp and 8.3% sodium hydroxide solution is filtered after the fibers have been previously swollen in a 17.5% NaOH solution, and the hemicellulose fraction which is contained in the short-chain material that dissolves. The hemicellulose fraction can be further subdivided into beta- and gamma-cellulose.

The division of the pulp into these three fractions is by a highly empirical procedure originally devised by Cross and Bevan in 1897, and which has been used since then to define alpha-, beta-, and gamma-cellulose.

The pulp is treated with a definite amount of 17.5% NaOH solution for 45 minutes. The concentration of the sodium hydroxide is then reduced to 8.3%, and the mixture treated for another 30 minutes. The alpha-cellulose is separated by filtration through a filter crucible, washed, dried, and weighed.

The total beta- plus gamma-fraction is determined volumetrically in an aliquot of the alkaline filtrate, after oxidation with dichromate. Another aliquot of the alkaline filtrate is acidified, filtered, and the gamma-fraction (that which remains in the filtrate) is similarly determined. This method is standardized as ASTM D558 and TAPPI T 203 os-61.

**NOTE.**—This standard for determining the alpha-cellulose, with some revisions to secure better reproducibility, but which, unfortunately, do change the results, is being preserved mainly for historical reasons.

TAPPI T 235 in the Standard Solubility of Pulp in Sodium Hydroxide is superior to this method for characterizing pulps, and its use is preferable for purchase specifications and for measuring the suitability of pulps for various dissolving processes.

The procedure described here is best suited to bleached pulps. Some unbleached pulps

<sup>32</sup> Report of Division of Cellulose Chemistry of the American Chemical Society, Ind. Eng. Chem., Anal. Ed., 1, 52, 1929.

<sup>33</sup> Doree, C., The Methods of Cellulose Chemistry, 2nd ed., D. Van Nostrand Co., New York, p. 363, 1947.

may prove so difficult to filter that they may require a prior chlorite or holocellulose treatment

For the determination of alpha cellulose in paper see TAPPI T 429 m p 18<sup>90</sup>

**Apparatus** Water Bath—At  $20.0 \pm 0.2^\circ\text{C}$  large size

**Filtering Crucible**—Low form 30 ml alkali resistant with fritted disc of coarse porosity (nominal maximum pore size 40 to 60  $\mu$ )

**Suction Flasks** for crucible two

**Glass Stoppered Weighing Bottle**—Large enough to hold the filtering crucible

**Glass Stirring Rod**—About 7 in long with one end flattened to a disc about 1 cm diameter

**Other Equipment** 100 ml graduate 250 ml beakers with watch glass covers 100 and 500 ml volumetric flasks 250 ml 500 ml and 1 liter Erlenmeyer flasks 10 ml and 50 ml pipets 250 ml glass stoppered graduated cylinder and 100 ml paper

**Reagents** Sodium Hydroxide Solution  $17.5 \pm 0.1$  g NaOH per 100 g of Solution—Dissolve a quantity of solid sodium hydroxide in an equal weight of distilled water cover and allow the suspended carbonate to settle which may take several days Decant or siphon off the clear supernatant liquid and dilute with CO free distilled water until the specific gravity at  $20^\circ/4^\circ$  is  $1.192 \pm 0.001$  (correction per  $^\circ\text{C}$  0.00051) Check the final dilution by titration with standard acid (1 Na CO<sub>3</sub> content of the diluted solution should not exceed 1 g per liter)

Sodium Hydroxide Solution 8.3 g NaOH per 100 g of Solution Dilute another portion of 50% NaOH with CO<sub>2</sub> free distilled water to a specific gravity of 1.091 0.001 at  $20^\circ/4^\circ$

Acetic Acid 2 N

Concentrated Sulfuric Acid 94–95% H<sub>2</sub>SO<sub>4</sub> (sp gr 1.84) Reagent Grade

Sulfuric Acid 6 N H<sub>2</sub>SO<sub>4</sub>

Potassium Dichromate Solution, 0.4 N—20 g K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> with 150 ml concentrated H<sub>2</sub>SO<sub>4</sub> per liter

Sodium Thiosulfate 0.1 N Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> Accurately Standardized

Potassium Iodide Solid KI Reagent Grade

Starch Solution 0.5% (or Thiodene Powder)

**Test Specimen**—Obtain a sample of pulp which is representative of the entire lot being tested weighing at least 10 g If in sheet form split then tear it into pieces approximately 5 to 10 mm across Do not cut with a pair of scissors or use a grinder Spread the torn pieces on a tray open to laboratory air for at least 24 hours to attain uniform moisture content At about the same time take composite specimens for the moisture and alpha cellulose determinations

**Procedure** Alpha Cellulose—During the procedure keep the sodium hydroxide solutions distilled water and acetic acid at  $20.0 \pm 0.2^\circ\text{C}$  this is conveniently done by placing them in flasks held in the water bath However the water used for the final rinse of the alpha cellulose residue need not be exactly  $20^\circ\text{C}$

Heat the fritted glass crucible and weighing bottle in the oven at  $105 \pm 3^\circ\text{C}$  to constant weight ( $\pm 0.5$  mg) place the crucible in its bottle and stopper tightly Cool in a desiccator for an hour or more Loosen the cover of the bottle momentarily to equalize the pressure and weigh to the nearest milligram

Weigh to the nearest 5 mg or less the equivalent of 3.0 g of moisture free pulp At about the same time weigh another portion and determine its exact moisture content according to ASTM D644-55 Transfer the specimen for the alkali treatment to a 250 ml beaker in the water bath Accurately measure 75 ml of the

17.5% NaOH solution into a graduate at 20°C. Wet the pulp with 15 ml. of the NaOH solution and macerate gently with the flattened glass rod for 1 min., add 10 ml. more and mix for 45 sec., then 10 ml. more and mix for 15 sec.; so that at the end of 2 min., 35 ml. of the NaOH have been added to form a slurry free from lumps, with the minimum amount of maceration. Stir and allow the mixture to stand for another 3 min. Without removing the beaker from the bath, add an additional 10 ml. of the NaOH solution, and mix with the flattened stirring rod for a total of 10 minutes, meanwhile adding the remaining 30 ml. of the NaOH solution in 10-ml. portions, after 2.5, 5, and 7.5 minutes. At the end of the 10 minutes, without removing the stirring rod, cover the beaker with a watch glass and leave the mixture in the water bath for 30 minutes more, a total of 45 minutes after adding the first portion of sodium hydroxide. Then add 100 ml. of distilled water at 20°C.; quickly and thoroughly mix and leave the diluted mixture in the water bath for a total period of 30 minutes, a total period of 75 minutes in contact with sodium hydroxide.

NOTE.—Contact with the resulting 8.3% NaOH, in which a small portion of the treated specimen is quite soluble, has been lengthened in order to avoid the uncertainty as to how much of this fraction is inadvertently dissolved during the dilution step.

Pour the contents into the tared fritted crucible on a clean suction flask. If suspended fibers are noticed in the filtrate, pass it through the cellulose mat again to clarify it. Rinse the beaker and residue with 25 ml. of 8.3% NaOH solution at 20°C. and quantitatively transfer all the fibers to the crucible. During the filtration, always keep the cellulose pad covered with solution to prevent drawing air through the pulp pad. Wash the filtered residue, using five 50-ml. portions of distilled water at 20°C. Set aside the filtrate (which should be less than 500 ml.) for the determination of beta- and gamma-cellulose.

NOTE.—It is assumed that the filtering procedure will occupy about 5 minutes. If the pulp is difficult to filter, taking over 5 minutes, decrease the 30-minute standing time for subsequent specimens of that pulp accordingly.

Place another suction flask in position and wash the residue in the crucible with an additional 400 ml. of distilled water, discarding the filtrate. Disconnect the suction tube, fill the crucible with 2 *N* acetic acid at 20°C. and allow the residue to soak for 5 minutes. Reapply the suction and draw off the acetic acid. Wash the residue with water until it is free from acid, as indicated by litmus paper.

Wipe the bottom and sides of the crucible with a dry towel and place it in an oven at  $105 \pm 3^\circ\text{C}$ . along with its weighing bottle. Dry to constant weight, then cool and weigh in its weighing bottle as before. Avoid prolonged heating because after it reaches a minimum, a gain in weight will occur.

Calculate the alpha-cellulose as a percentage, based on the moisture-free pulp.

*Correction for Ash and Lignin.*—Correct results from those pulps with appreciable ash, and from unbleached pulps for their ash and lignin contents. Subtract these quantities from the weight of the alpha-cellulose, to obtain the corrected value.

**Beta- and Gamma-Cellulose.**—Quantitatively transfer the alkaline filtrate from the suction flask to a 500-ml. volumetric flask, make up to the mark with distilled water, and mix.

Determine the cellulose dissolved in the alkali by oxidation with the dichromate solutions as follows:

With a pipet transfer 50 ml of the filtrate to a 500 ml Erlenmeyer flask. Add 10 ml of 0.4 N  $\text{K}_2\text{Cr}_2\text{O}_7$  and then, carefully, 90 ml of concentrated  $\text{H}_2\text{SO}_4$ . If the sulfuric acid is of lower concentration than 94%, the temperature will not reach 125 to 130°C during the oxidation. Swirl to mix, and apply heat to maintain a solution temperature of  $127 \pm 2^\circ\text{C}$  for a 10 minute period to complete the oxidation. Use of a reflux system for the flask is desirable. Cool the flask to room temperature and quantitatively transfer the solution to a 1 liter Erlenmeyer flask using 500 ml of distilled water. Add approximately 2 g of solid KI swirl to dissolve, and allow it to stand for 5 minutes. Titrate with the 0.1 N  $\text{Na}_2\text{S}_2\text{O}_3$  solution adding the starch indicator near the end point when the yellow color of the iodine has nearly disappeared. The end point occurs when the color of the solution changes from deep blue to light green. Make a blank titration substituting a 50 ml portion of the 0.5 N NaOH for the filtrate and using approximately the same temperature and time to complete the titration. Calculate the percentage of beta plus gamma cellulose as

$$\frac{(V_2 - V_1) \times N \times 6.85}{W}$$

where  $V_1$  = ml of  $\text{Na}_2\text{S}_2\text{O}_3$  consumed in the titration of the filtrate

$V_2$  = ml of  $\text{Na}_2\text{S}_2\text{O}_3$  consumed in the titration of the blank

$N$  = normality of the  $\text{Na}_2\text{S}_2\text{O}_3$  solution

$W$  = moisture-free weight of the pulp used

6.85 = mg of cellulose corresponding to 1 milliequivalent of  $\text{K}_2\text{Cr}_2\text{O}_7$

Note.—Theoretically 1 ml of  $\text{K}_2\text{Cr}_2\text{O}_7$  corresponds to 6.75 mg of cellulose or polysaccharide under the less ideal conditions of the oxidation described above, 1 milliequivalent corresponds to 6.85 mg.

The equivalence factor for the conditions and solutions employed for each occasion may be determined as follows:

Without heating dissolve 0.2 ± 0.001 g (moisture free) of high quality bleached cotton linters or ashless filter paper in 40 ml of 72%  $\text{H}_2\text{SO}_4$  and in a 100 ml volumetric flask dilute to the mark with more 72% acid. Immediately thereafter, pipet duplicate 10 ml aliquots of the cellulose solution into a pair of 500 ml Erlenmeyer flasks, add 40 ml 0.5 N NaOH to each and another 10 ml portion of the NaOH to another flask as a blank. Oxidize and titrate the blank and each flask containing the 20 mg of cellulose as described above. Suppose the results are  $I_3$  and  $I_4$  ml respectively, then the equivalence factor (milligrams of cellulose per milliliter of  $N$  solution) or milligrams of cellulose per 10 ml of the 0.1 N  $\text{Na}_2\text{S}_2\text{O}_3$  as used—the portion replaced by cellulose having been oxidized is  $200/(I_3 - I_4)$ .

Take care that the 10 ml pipet used to deliver the cellulose aliquot is calibrated for the delivery of that solution, since it is more viscous than water. (Using the same 10 ml pipet as was used for the specimen will minimize the possible error.)

Alternatively in place of the KI and  $\text{Na}_2\text{S}_2\text{O}_3$  titration after cooling the oxidized specimen to room temperature add 50 ml of water to the specimen and to the blank, cool again to room temperature add 2 to 4 drops of ferroin indicator (15 g of  $\alpha$ -phenanthroline monohydrate—or 16 g of the hydrochloride—plus 0.7 g of  $\text{FeSO}_4$  dissolved in water and diluted to 100 ml) and titrate with a freshly standardized 0.1 N solution of ferrous ammonium sulfate to a purple color. In the calculation above  $I_1$  and  $I_2$  will represent the volumes of ferrous ammonium sulfate used for the specimen and blank, respectively. An electrometric titrimeter is preferable for this titration.

If the alpha cellulose content is less than 91%, there is not sufficient  $\text{K}_2\text{Cr}_2\text{O}_7$  in 10 ml of the 0.4 N reagent to oxidize the cellulose in the 50 ml aliquot of beta and gamma cellulose taken originally from the 500 ml flask. Use a 25 ml aliquot and 25 ml of 0.5 N NaOH for the blank titration so that the acid to total solution ratio remains constant.

Gamma Cellulose.—Transfer exactly 190 ml of the original alkaline filtrate to a 250 ml glass stoppered graduated cylinder. Add a few drops of methyl orange

and fill the graduate to the 240-ml. mark with 6 *N* H<sub>2</sub>SO<sub>4</sub>, stopper the cylinder, and invert several times to mix. Adjust to the acid side if necessary by the further addition of H<sub>2</sub>SO<sub>4</sub>. After cooling, dilute to the 250-ml. mark with distilled water, mix, and let stand at room temperature until the beta-cellulose has settled. This usually requires 16 hours.

Carefully decant the clear solution through a dry folded filter paper into a dry 250-ml. beaker, discarding the first 50 ml. Determine the gamma-cellulose in the filtrate by oxidizing a 50-ml. portion with 10 ml. of dichromate as described above for the beta- plus gamma-cellulose. Make a blank test by substituting 50 ml. of the 0.5 *N* NaOH for the filtrate.

Calculate the gamma-cellulose as a percentage of the moisture-free pulp as:

$$\text{gamma-cellulose} = \frac{(V_2 - V_1) \times N \times 6.85 \times 1.316}{W}$$

where 1.316 is the aliquot factor, and the other symbols are as before.

Calculate the percentage of beta-cellulose by difference between this and the beta- plus gamma-cellulose.

**Report.**—Report the alpha-, beta-, and gamma-cellulose as percentages of moisture-free pulp, to the nearest 0.1%, and if the pulp is unbleached, state whether or not the results are corrected for lignin and ash.

## PITCH IN WOOD PULP

This method is standardized as TAPPI T 204 m-54.

**Preparation of Sample.**—If the pulp is sufficiently wet, it shall be separated into thin layers and allowed to dry in the air overnight. If the pulp is too dry to separate, it shall be soaked in water, then separated into layers and allowed to dry overnight. The layers shall then be cut into pieces about 2 by 4 in., and 5 g. weighed out for each extraction. Pieces shall be creased alternately parallel to the shorter direction so that they may be closed up like a camera bellows. This is very necessary to keep the surfaces apart in the extractor and to facilitate rapid extraction. (If preferred, the pulp may be shredded before extraction and packed into the extractor loosely.)

Where extreme accuracy is desired, the moisture shall be determined on a separate portion of the air-dried pulp by drying a weighed sample to constant weight at 105 ± 3°C., and the pitch percentages subsequently obtained shall be corrected to the air-dry basis by dividing the actual results by 1-*M*/0.90, where *M* is the percentage of moisture expressed as a decimal. For ordinary purposes, however, the strips dried overnight may be considered in the air-dry condition.

**Ether Extract.**—Accurately weigh 5 g. of the pulp prepared as previously described, place it in a Soxhlet or a continuous extractor connected to an unweighed Erlenmeyer or Soxhlet flask, and extract with sulfuric ether for at least 16 hours with the ether boiling rapidly.

Filter the ether solution through a wad of absorbent cotton in the bottom of a glass funnel, washing the funnel and the cotton finally with a little ether, and collect the filtrate in a weighed Soxhlet flask. Then evaporate the solution in the flask, dry the residue on the steam bath until the ether is removed, and finally dry in the oven at not over 105°C. to constant weight. Calculate the weight of residue to percentage of the air-dry pulp and report as ether-soluble pitch.



These specifications are in addition to those for the dimensions and do not alter the dimensions.

The top of the tube is closed with a rubber stopper, carrying another capillary which has a ground-glass stopcock. The bottom capillary is closed with a rubber tube and clamp. Each tube has a wedge-shaped cylinder, Fig. 38-12, the bottom of which is notched. The cylinder, made from  $\frac{1}{4}$ -in. steel or Monel rod, is 2.5 cm. long.

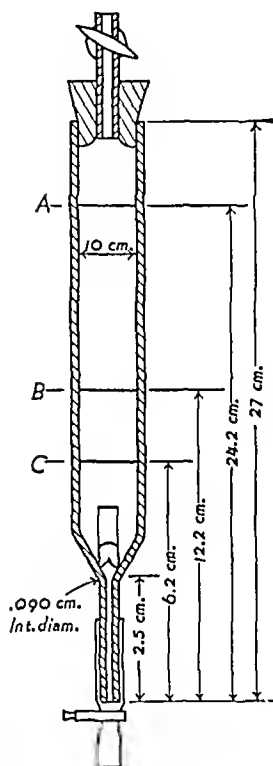


FIG. 38-10. Viscosity tube.

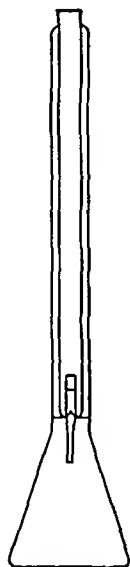


FIG. 38-11.  
Jacket.

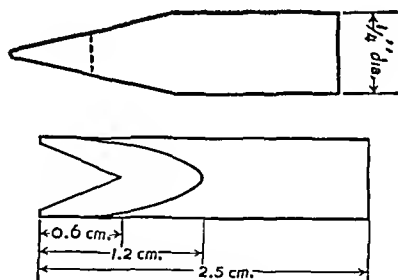


FIG. 38-12. Wedge.

The glass jacket, Fig. 38-11, supports the viscosity tube in the thermostat. The jacket is so constructed that it supports the tube on three glass points at the bottom and is a sliding fit at the top.

**Calibration of Viscosity Tube.**—The volume of the tube is obtained as follows: Fill the tube containing the wedge with water, put the rubber stopper tightly in place and force the excess water out through the capillary. (The rubber stopper must be replaced periodically by a fresh one, determining the new volume each time.) Open the stopcock and drain the contents into a buret, noting the time in seconds for the meniscus to fall from line *A* to line *C*. Read the volume of the water delivered to the buret and take the average of several determinations as the volume of the tube.

The tube constants *C* and *h* are determined from the formula:

$$\eta = \frac{d}{C} (t - k) \quad (1)$$

where  $\eta$  = viscosity in centipoises

$d$  = specific gravity of the solution

$t$  = time in seconds for meniscus to fall from line  $A$  to  $C$ ,

$C$  = tube constant

and  $k$  = gravity constant

The constant  $C$  is first determined with standard glycerine solution of approximately 1.21 sp gr (85% solution) at 20.0°C. The specific gravity must be accurately determined with a pycnometer. The viscosity may be obtained from a curve

TABLE 38.1<sup>28</sup> VISCOSITY OF GLYCERINE-WATER SOLUTIONS

Specific Gravity at 20.0°C	Viscosity in Centipoises at 20.0°C	Specific Gravity at 20.0°C	Viscosity in Centipoises at 20.0°C
1.0000	1.009	1.2155	74.780
1.1014	3.734	1.2240	110.800
1.1699	15.360	1.2463	409.300
1.1848	23.540	1.2568	871.700
1.2057	49.670		

<sup>28</sup> International Critical Tables, Vol. 5, p. 23.

drawn from Table 38.1. In this case constant  $k$  may be disregarded since the time of efflux is long. The formula then becomes

$$C = \frac{dt}{\eta} \quad (2)$$

from which the tube constant is calculated. The gravity constant  $k$  is determined by repeating the operation with water at 20.0°C and substituting for  $C$  in formula (1) the value found above as well as  $d = 1$  and  $t = 1$ . The formula then becomes

$$k = t^2 - Ct \quad (3)$$

**NOTE**—The Hartman-Leddon Company, 6003 Girard Avenue, Philadelphia 12, has prepared four mineral oil reference standards for the calibration of the viscosity tubes used in this method. These reference standards are approximately 20 and 50 centipoises with a statement of the actual measurement within a tolerance of error of 0.5 centipoise.

**Reagent Cuprammonium Solution**—Freshly prepare the cuprammonium solution at least every 2 months as follows. Place clean copper turnings in a glass tube 2½ in. long and 4 in. in diameter surrounded with ice. (The turnings must be previously cleaned by washing in dilute HCl.) Pour in concentrated NH<sub>4</sub>OH (26–28% NH<sub>3</sub>) containing 2 g. of cane sugar per liter until the tube is nearly full. Bubble air which is passed through a wash bottle containing concentrated NH<sub>4</sub>OH through the solution for several hours until the desired Cu concentration is reached. Analyze the solution for Cu and NH<sub>3</sub> and make the proper adjustments. The Cu concentration shall be 14.8 to 15.2 g. per liter, the NH<sub>3</sub> concentration 190 to 210 g. per liter.

The course of the reaction can be followed by estimating the Cu content colorimetrically by comparing with a standard, both diluted 50-fold.

Determine the Cu and  $\text{NH}_3$  in the cuprammonium solution as follows:

(a) *Copper*. Pipet 10 ml. of the cuprammonium solution into a 250-ml. Erlenmeyer flask, and dilute with 25 ml. of water. Boil the solution until no more  $\text{NH}_3$  is given off. Add 5 ml. of  $\text{HNO}_3$  (1:1) and boil until red fumes are expelled. Then add 2 ml. of bromine water and boil until the Br is all expelled. Remove from the heat, dilute to 75 ml., and carefully add  $\text{NH}_4\text{OH}$  until the solution becomes just alkaline (blue), but not more. Add a slight excess (4 or 5 ml.) of glacial acetic acid, cool to tap water temperature, and add 10 ml. of 30% KI solution. Titrate with 0.1 *N* thiosulfate solution until the yellow color of free iodine is nearly gone, then add starch indicator and continue the titration cautiously until, on the addition of another drop, the blue color due to free I disappears.

*Calculation*.—Copper content of cuprammonium solution in grams per liter = ml. 0.1 *N* thiosulfate  $\times$  0.636.

(b) *Ammonia*. Pipet 2 ml. of the cuprammonium solution into 50 ml. of normal  $\text{H}_2\text{SO}_4$  solution, keeping the tip of the pipet beneath the surface of the liquid. Titrate the excess acid with normal NaOH, using methyl red indicator.

*Calculation*.— $\text{NH}_3$  content of cuprammonium solution in grams per liter = (50 — ml. NaOH)  $\times$  8.5 — 0.536 *C*, where *C* = copper concentration in grams per liter.

Care should be taken that no liquid adheres to the outside of the pipet before it is inserted into the acid solution. The correction factor (0.536 *C*) is made for the alkalinity of the copper hydroxide.

*Test Specimen*.—A representative pulp sample in the air-dry condition shall be shredded by means of a mechanical shredder or a coarse steel file. Wet pulp may be made into several handsheets, dried in the oven at  $105 \pm 3^\circ\text{C}$ . for 3 minutes, and then shredded.

The air-dry pulp shall be placed in a stoppered bottle and the moisture content determined on a portion of it. The weight of air-dry pulp equivalent to 1 g. of moisture-free pulp for each 100 ml. of tube volume shall be calculated for each tube, and the proper amount of sample weighed out for the tube employed.

*Procedure*.—Take the calculated weight of moisture-free pulp to give a 1% solution and loosely roll it into the form of a cigarette in a strip of hard-surfaced paper such as glassine; then moisten this roll with 5 or 6 drops of water and slide it from the paper into the viscosity tube. Siphon the cuprammonium solution into the bottom of the tube by means of the rubber tubing at the bottom, until it is two-thirds full. Quickly break up the pulp roll with the aid of a thin glass stirring rod. Add the remainder of the solution at the top, scrape the rod clean, and insert the stopper. Force the excess solution through the capillary and close the stopcock. Wrap the viscosity tube in black cloth, and place it on a wheel rotating 3 or 4 r.p.m., so that the metal wedge falls freely through the solution as the tube rotates. The pulp should be well broken up so that the metal wedge will fall through the full length of the tube before the tube is put on the rotating wheel. Allow 15 hours rotation (overnight) for the complete dispersion of the pulp.

Place the tube in the thermostat at  $20^\circ\text{C}$ . until equilibrium is established. Remove the rubber tubing from the capillary and place the tube in position in the jacket, which remains in the thermostat. Remove the rubber stopper, allowing the pulp solution to flow through the capillary. Note the time in seconds (*t*) for the meniscus to pass between the marks *A* and *C*, and calculate the viscosity of the

solution from the formula

$$V = \frac{d}{C} \left( t - \frac{k}{t} \right) \quad (1)$$

in which  $d$  the specific gravity of the pulp solution is 0.96  $C$  and  $k$  are constants found. Simplifying the equation becomes

$$V = C \left( t - \frac{k}{t} \right) \text{ where } C^1 = \frac{0.96}{C} \quad (4)$$

Inspection will show when the expression  $k/t$  may be disregarded as is usually the case with unbleached pulps of high viscosity.

The tubes may be cleaned by immersion in nitric acid (1:1).

**Report.** Results shall be reported in terms of centipoises and represent the average of at least two tests.

**Precision.** Duplicate samples should check within 2% on bleached and 3% on unbleached pulps.

## WATER SOLUBILITY OF PULP<sup>39 40 41</sup>

This method is standardized as TAPPI T 207 m 54.

### COLD WATER SOLUBILITY

**Apparatus.** The special apparatus required consists of a suction filter flask and a rubber flange for the crucible and funnel.

**Specimen.**—The specimen shall consist of about 2 g of air dry pulp accurately weighed.

**Procedure.**—Place 2 g of air dry material the moisture content of which has been determined on a separate portion in a 400 ml beaker and cover with 300 ml of distilled water. Let the mixture digest at room temperature with frequent stirring for 48 hours. Transfer the material to a tared alundum crucible wash with cold distilled water and dry to constant weight at  $105 \pm 3^\circ\text{C}$ . Drying usually requires approximately 4 hours. Place the crucible in a stoppered weighing bottle cool in a desiccator over concentrated sulfuric acid and weigh.

**Report.** The amount soluble shall be reported as a percentage of the moisture free weight of the pulp.

### HOT WATER SOLUBILITY

**Apparatus.**—The special apparatus required is a constant level boiling water bath.

**Specimen.**—The specimen shall consist of about 2 g of air dry pulp accurately weighed.

**Procedure.**—Digest 2 g of air dry material the moisture content of which has been previously determined on a separate portion with 100 ml of distilled water in a 200 ml Erlenmeyer flask provided with a reflux condenser. Place the flask in a boiling water bath the water level of which is maintained constant just above

<sup>39</sup> Schoiger, A. W. *Chemistry of Cellulose and Wood*. McGraw Hill, New York, p. 506, 1926.

<sup>40</sup> Hawley and Wise. *Chemistry of Wood*. Chemical Catalog Company, New York, p. 151, 1926.

<sup>41</sup> Bray, M. W. *Paper Trade J.* 87, 59-68, Dec. 20, 1928.

the solution in the flask, by means of a constant-level apparatus. After boiling gently for 3 hours, transfer the contents of the flask to a tared alundum crucible, wash with hot water, dry at  $105 \pm 3^\circ\text{C}$ ., cool in a desiccator over concentrated  $\text{H}_2\text{SO}_4$  and weigh in a stoppered weighing bottle.

Report.—The amount soluble shall be reported as a percentage of the moisture-free weight of the pulp.

### WEIGHING, SAMPLING, AND TESTING PULP FOR MOISTURE <sup>42</sup>

The determination of moisture in wood pulp varies with the form in which it is manufactured, and the methods selected for moisture testing are specified for each given form or kind of pulp. These include: (1) baled pulp: dried sheets, shredded pulp, hydraulic pressed laps; (2) roll pulp; (3) loose lap pulp: wet laps, hydraulic pressed laps; (4) double-press wet-machine pulp in sheets. This method is standardized as TAPPI T 210 m-58.

NOTE.—Other conditions also affect the testing of pulp, such as the place of testing, the time elapsed before testing, and the quantity of pulp. The place of testing may be at mill during manufacture; at dock during transfer from car to ship for export, or vice versa; at receiving point for incoming car lots or shiploads. The pulp may be freshly made or stored in warehouses or open piles.

*Apparatus. Sampling Tool.*—For testing baled dry pulp, a boring tool which cuts a disk about 4 in. in diameter is used. For baled shredded pulp, a special tool (Crossley Sampling Tool made by Thompson Mfg. Co., Lancaster, N. H.) similar to a cork borer is used to cut a sample  $1\frac{1}{4}$  in. in diameter and to a depth of 4 in.

*Template.*—For the wedge method a template with an apex angle of approximately 4 to 9° is desirable. This is preferably made of brass and should have a length of about 18 in.

*Laboratory Scales.*—Scales used for weighing pulp samples shall show a sensitivity of 0.1% of maximum load. For example, if 1 kg. (2.2 lb.) of pulp sample is taken, the scales must show a decided deflection by the addition of 1 g. to the load.

*Drying Oven.*—Any suitable laboratory drying oven may be used for drying samples to constant weight. A temperature recorder is recommended to measure the temperature throughout the test. The temperature throughout the oven shall not exceed  $108^\circ\text{C}$ . ( $226.4^\circ\text{F}$ .) at any time during the test, and shall be maintained at  $105 \pm 3^\circ\text{C}$ . ( $221 \pm 5.4^\circ\text{F}$ .) during the last two hours of drying time.

*Samples.*—No one method of sampling is suitable for all the different forms of pulp. The various sampling methods and their application are as follows, their fuller description being included under the procedure to which they apply:

*Strip Method.*—The strip method, while well adapted to mill sampling of unpressed wet laps or roll pulp, is not suitable for frozen lap pulp at receiving point.

*Boring Method.*—The boring method, while well adapted to the sampling of baled pulp and rolled pulp, is not suited to the sampling of wet lap pulp of under 36% moisture-free content (40% air-dry).

<sup>42</sup> Official Rules for Weighing, Sampling and Testing Wood Pulp for Moisture, Approved by the Certified Pulp Testers' Bureau of the American Paper and Pulp Association, Association of American Wood Pulp Importers, and Technical Association of the Pulp and Paper Industry.

**Wedge Method**—The wedge method or any other method which involves the breaking open of bales is not suitable for referee sampling of pulp at dock since transportation companies decline to handle broken bales and rebaling with an ordinary handpress is not practicable.

**Number of Samples**—Sufficient and representative samples from individual units must be taken to ensure a fair average of the lot. This is especially necessary where grab samples from opened bales are taken.

**Procedure Determination of Gross Weight of Pulp**—As all pulp is invoiced on the basis of air dry tons rules for the determination of the moist weight of the pulp are just as important as rules for sampling and testing and the moist weight shall always be determined by one of the following methods.

**Railroad Weight**—Railroad weight of entire car uncoupled and weighed separately when the tare of the empty car is actually determined by weighing it. (This does not mean the routine bill of lading railroad weight but an actual weighing upon railroad scales properly supervised.)

**Certified Weight**—Weight of entire car lot as certified by officially recognized weighing bureau issuing weigh master's certificate of weight.

**Weighting by Truck and Tested Scales**—Weight of lot by sum of weights of truck loads passing over accurately tested scales during loading or unloading less the tare of the trucks.

**By Calculation from Average Weight of Parcels**—Weight of lot determined by multiplying the actual number of bales or rolls in the shipment as determined by accurate count by the average weight of the bales or rolls weighed and sampled. In domestic roll or wet bale pulp the variation in weight between individual rolls or bales is often so great that it may be necessary to weigh the entire shipment. In the case of roll pulp or shredded pulp at least 25% of the rolls and preferably the entire shipment should be weighed.

The accurate weight of all bales sampled shall be ascertained before sampling no unweighed bales shall be sampled (roll pulp and shredded pulp excepted). Whenever bales are numbered their numbers shall be listed in addition to their weights.

Only normal bales shall be sampled. Reject as abnormal those bales obviously damaged or whose weight differs from the average gross weight as determined at the time of testing by more than 10% plus or minus.

**Scales**—Scales will be accepted as accurate (1) when verified by standard test weights or (2) when verified by weighing a known or measured volume of water.

Scales for weighing bales shall be provided with 1 lb divisions. They shall have such accuracy that after having been balanced they will show a variation of not more than 1 lb when a 400 lb reference weight is placed upon them and the load manually increased and decreased temporarily.

**Handling of Samples**—The samples taken shall be immediately deposited in a metal can with tightly fitting cover, and the net weight obtained as soon as practicable. In case of an unavoidable delay between the time of taking the samples and weighing if an airtight container is not available, use a cover, the edges of which shall be sealed with friction tape or the equivalent.

**Weighting and Drying of Samples**—Both moist weight and dry weight shall be obtained upon the same scales with the same weights.

All the samples taken shall be dried out for the test. After weighing the moist samples, these shall be placed in a suitable oven and dried to constant weight at

a temperature of not less than 99°C. (210°F.) and not more than 108°C. (226°F.). A minimum allowable temperature of at least 102°C. (216°F.) shall be maintained during at least the last 3 hours of drying. The hot samples shall be weighed in the oven or in closed containers immediately after being withdrawn from the oven, taking care to avoid convection currents while weighing. Two successive weighings at least 3 hours apart shall not show a variation greater than 0.1% of the moist weight of samples, and the total of the minimum weights shall be taken as the final moisture-free weight.

To calculate the percentage of moisture-free pulp, divide the weight of moisture-free pulp by the moist weight and multiply by 100. To calculate the air-dry percentage, divide the percentage of moisture-free pulp by 0.9. Multiply the moist weight by this air-dry percentage and divide by 100 to obtain the weight of air-dry pulp.

**Testing at Pulp Mill.**—The strip method shall be used for sampling pulp coming from the wet machine or from driers in continuous web. Cut a 2- or 3-in. uniformly wide strip across the entire width of web coming from the machine. One such sample shall be taken from the wet machine for every 2000 lb. wet weight production. For web-dried pulp, one such sample shall be taken for every fifth bale or roll of production.

**Testing on Dock or Receiving Point. Boring Method.**—This is suitable for sampling (1) baled pulp in sheets, (2) roll pulp, (3) baled shredded pulp having 50% moisture or less, and (4) hydraulic pressed laps having 64% moisture or less.

**Baled pulp in sheets:**

(a) Number of bales to be sampled: On lots of 3000 bales or less, 10% shall be taken, except by agreement, but never less than 15 bales. Samples shall be drawn from only sound and intact bales from different sections of the entire shipment.

(b) Details: The samples shall be taken by boring into each bale to a depth of 3 in., with a special tool which cuts disks about 4 in. in diameter. The disks shall be removed and 10 of them taken as a sample, selected as follows: one disk from second sheet from the wrapper; two disks 1 in. deep; three disks 2 in. deep; four disks 3 in. deep.

The holes to be bored shall be so located that in each series of five successive bales they will represent a portion extending diagonally across the bale. Each bale shall be bored but once, the first bale at the corner, the edges of the cut being at a distance of 1 in. from the edge of the bale. The second cut shall then be made half-way between the corner and the center of the bale; the third bale shall be cut at the center; the fourth bale half-way between the center and the corner; and the fifth bale in the opposite corner in a position corresponding to the first. In case binding wires or straps interfere with the exact location of cuts, borings shall be made as near the prescribed location as possible.

**Roll pulp:**

(a) Number of rolls to be sampled: At least 10% of the lot, but not less than 30 rolls. Where possible to determine, the same proportion of outside rolls to center rolls should be maintained as coming from the machine.

(b) Details: The edge of the first hole shall be 2 in. from one end; holes in succeeding rolls shall be spaced successively one-fifth of the distance across the roll as in bale sampling, traveling toward the opposite end of the roll. Selection of discs shall be in accordance with bale boring as given above.

### Baled shredded pulp

(a) **Standard method using sampling tool** The wet weight of the lot shall be obtained by weighing at least 25% of the bales and preferably the entire shipment. When the total weight is to be determined by weighing a portion of the shipment, select sound intact and undamaged bales at regular intervals throughout the lot, make a careful count of the total number of bales, and calculate the total wet weight from the average weight of bales weighed.

Take the sample by boring into the bale with the special tool (Crossley Sampling Tool) to a depth of at least 4 in. The entire sample shall be taken for drying.

The holes to be bored shall be located so that in five successive bales they will represent a portion extending diagonally across the side of the bale. Bore each bale selected for sampling only once. The first bale shall be bored at the corner of the bale, the edge of the cut being at a distance of 2 in. from the edge of the bale. The second cut shall be made halfway between the corner and the center of the bale, the third bale shall be cut at the center, the fourth bale halfway between the center and the corner, and the fifth bale in the opposite corner in a position corresponding to the first cut.

(b) **Optional grab sample method** (required in the case of shredded pulp with more than 50% moisture) Ten per cent of each shipment, i.e. each tenth bale as it arrives at the plant of the purchaser shall be sampled. The bales are numbered as they are chosen, and each bale is weighed on accurate scales. In rotation the bales are designated as A, B, C, D, and E, then each bale is broken open by cutting the binding wires. A grab sample of 500 g. plus or minus 15 g. shall be taken from a point in the bale according to its general letter designation, thus:

The A sample is taken at a point 4 in. down, 4 in. from the edge and 4 in. into the bale. B sample is taken 8 in. in each direction. C sample 12 in., D sample 16 in., and E sample 20 in.

**Strip Method**—This is suitable for sampling (1) wet machine pulp not hydraulically pressed, (2) unpressed lap pulp, and (3) roll pulp. All sample strips shall be the same width.

### Wet machine pulp, not hydraulically pressed

Cut a strip 2 or 3 in. wide through the center of the sheet across the machine direction. Samples shall be taken throughout the lot, and the frequency of sampling shall provide at least one strip for each 2000 lb. of wet pulp.

### Lap pulp, unpressed

Cut a 2 or 3 in. strip through the center of the lap across the machine direction, (see Fig. 38.13) to a depth halfway through. Samples shall be taken throughout the car lot, and the frequency of sampling shall provide at least one sample for each 2000 lb. of wet pulp.

### Roll pulp

For roll pulp, take a test strip of 2 or 3 in. in width across the face of the roll from the second layer, and 4 other similar strips from layers located at least 1 in. or deeper from the outside layer.

**NOTE**—While the strip method is quite commonly used for sampling hydraulic pressed lap pulp, this method is known and has been proved to give high results both by calculation of ratio of wet edge to dry center of sample compared with the ratio of wet edge to dry center of total lap, and by repeated actual tests comparing the sample so taken with moisture tests on the whole lap.



*Wedge Method.*—This is suitable for sampling (1) lap pulp; (2) hydraulically pressed lap pulp; and (3) baled pulp in sheets when the bales can be conveniently opened.

This method is admittedly accurate when followed in exact details. The principal objections to its adoption as the only standard for lap pulp are the practical difficulties in getting nontechnical samplers to space the wedge cuts accurately. As an alternate method, the committee recommends the following modified wedge method, which has been proved by experience to give results well within practical limits of accuracy.

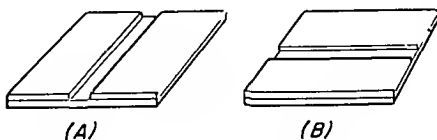


FIG. 38-13. Strips from Unpressed Lap Pulp.

The angle of the wedge shall be the same throughout as measured by a template.

#### Lap pulp:

For lap pulp a wedge sample shall be cut from every 2000 pounds wet weight when piled loose in the car, the center of the wedge to be at the center of the lap. Depth of cut: half through the lap. Positions of cuts: these shall start at the middle of the closed edge of the lap as the first position. Successive laps shall be cut going round clockwise as shown in Fig. 38-14.

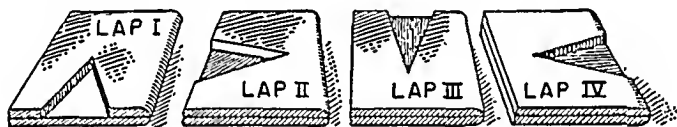


FIG. 38-14. Wedges from Laps.

#### Hydraulically pressed bales:

For hydraulically pressed bales it is convenient that the total number of bales sampled and weighed be a multiple of 20. The total number of bales weighed and sampled shall be at least  $2\frac{1}{2}\%$  of large lots and 5% of small lots (less than 1000 bales). From 20% of the bales sampled, withdraw the middle lap. From 40% of the bales sampled, withdraw the lap halfway between the outside and the center. From 35% of the bales sampled, withdraw the lap next to the outside. From 5% of the bales sampled, withdraw the outside lap.

Folded laps which are withdrawn from the outside of the bales shall be sampled on that side which formed the surface of the bale.

#### Baled pulp sheets:

For baled pulp sheets, the bales shall be sampled as for hydraulically pressed laps, using the first sheet below the wrapper as the outside layer.

*Precaution.*—The accuracy of weight and moisture determinations is dependent upon the taking of representative samples. The latter should be drawn only from sound, intact, and undamaged bales and from different sections of the entire shipment. Bales previously sampled should not be considered as sound or intact. No unusual conditions should prevail in the selection of bales.

*Retests in Case of Dispute.*—In case of dispute, a retest shall be made either by one approved analyst acting for and mutually agreed upon by both parties, or a

joint test shall be made by approved analysts representing both parties and mutually agreed upon by them. In case of a joint test both analysts or their authorized representatives shall be present during the sampling and weighing and subsequent testing of samples but only one set of samples shall be obtained from the bales weighed and these samples shall be dried in an oven approved by both analysts. Retests coming within 1% of the original air-dry weight of pulp as invoiced will be deemed to uphold the original invoice. When retests show a greater variation than 1% adjustments shall be made upon the actual basis of such retest. In all cases expenses incidental to the retest shall be paid by the party in error.

Retests shall not be made on pulp which has been unduly exposed to the weather or other unusual conditions of moisture or heat, except by special agreement between shipper and consignee.

Whenever possible in all cases of dispute, the shipment should be kept intact. In no case shall there be less than 50% of the lot presented for retest.

### ASH IN PULP

The ash content of pulp is defined as the residue remaining after ignition at  $575 \pm 25^{\circ}\text{C}$  ( $1067 \pm 45^{\circ}\text{F}$ ) for 3 hours, or longer if necessary to burn off all the carbon. It is a measure of mineral salts and inorganic foreign matter in the pulp but it is not necessarily quantitatively equal to them. Pulp, like wood, is ashed at lower temperature than is paper ( $925^{\circ}\text{C}$ ), to minimize the volatilization of inorganic compounds. This method is standardized as TAPPI T 211 m 58.

**Apparatus** Crucible—A platinum crucible or dish with lid or cover is recommended. If platinum is not available silica may be used.

Analytical Balance—Having a sensitivity of 0.1 mg with class S weights.

Electric Muffle Furnace—Adjusted to maintain a temperature of  $575 \pm 25^{\circ}\text{C}$ .

**Test Specimen**—Obtain a representative sample of the pulp. If from a shipment take a small portion from each bale sampled for weight and moisture in accordance with T 210 m (p 1761). Weigh out a representative portion of the sample for ashing preferably in duplicate. The size of the specimen required for each ash determination depends on its ash content and should be adjusted so that the weight of the ash will not be less than 10 mg and preferably not over 20 mg (see Table 38.2). If the amount of moisture in the sample is not known, determine it by drying a representative portion to constant weight at  $105 \pm 3^{\circ}\text{C}$ .

TABLE 38-2 APPROXIMATE SIZE OF SPECIMEN

Percentage Ash	Moisture-Free Pulp, g.
Over 0.5	5
0.20 to 0.50	10
0.12 to 0.20	20
0.08 to 0.12	30
0.04 to 0.08	40
Less than 0.04	50

**Procedure.**—Carefully clean the empty crucible and cover, if used, and ignite to constant weight in a muffle furnace at  $575 \pm 25^{\circ}\text{C}$ . After ignition cool slightly and

place in a desiccator, preferably containing indicating-grade, anhydrous alumina. When cooled to room temperature, weigh the ignited crucible on the analytical balance to the nearest 0.1 mg.

If of a suitable size, place all the specimen in the crucible and burn the pulp directly over a low flame of a Bunsen burner (or preferably on the hearth of the furnace) until it is well carbonized. If the crucible is too small to hold the entire specimen, gently burn the portion added and add more as the flame subsides. Take care not to blow portions of the ash from the crucible. Continue heating with the burner only as long as the residue burns with a flame. When the flame has died down, place the crucible in the furnace at  $575 \pm 25^{\circ}\text{C.}$  for a period of at least 3 hours, or longer if needed to burn away all the carbon.

When ignition is complete, as indicated by the absence of black particles, remove the crucible from the furnace, replace the cover and allow to cool somewhat. Then place in a desiccator and cool to room temperature. Reweigh with the ash to the nearest 0.1 mg. and calculate the percentage based on the moisture-free weight of the pulp.

Report.—Report the ash as a percentage of the moisture-free pulp to two significant figures, or to only one figure if the ash is less than 0.1%.

Precision.—The results of duplicate ash determination should be suspect if they differ by more than that indicated in Table 38-3.

TABLE 38-3. PERMISSIBLE DEVIATIONS BETWEEN DUPLICATES

<i>Weight of Ash, mg.</i>	<i>Maximum Permissible Difference, mg.</i>
20-50	2
5-20	1
Less than 5	0.5

*Additional Information.*—1. The ash so obtained usually is not fused to the platinum dish and is easily dissolved in dilute hydrochloric acid. It may be used subsequently for the determination of its constituents, such as iron, copper, and calcium.

2. Iron chlorides, if present, may be partially volatilized under the conditions specified.

3. Since the ignition temperature affects the weight of ash, only values obtained at  $575 \pm 25^{\circ}\text{C.}$  should be reported as being in accordance with this standard.

4. A value for sulfated ash may be found useful. However, a carefully controlled procedure is required, and the result would not be in accordance with this standard.

5. In this revision, the temperature of ignition has been specified at  $575 \pm 25^{\circ}\text{C.}$ , being the same as in TAPPI Standard T 15 m, Ash in Wood (p. 1738).

## ONE PER CENT CAUSTIC SODA SOLUBILITY OF PULP

This method determines the resistance of a pulp sample to solution by hot dilute alkali. In general, the less the chemical degradation of pulp, the lower is its alkali solubility. The bulk of the material dissolved consists of pentosans and other carbohydrates which are less resistant to chemical action than cellulose, and of cellulose which has been partially broken down during the process of preparation. These are the materials which in part make up the fractions known as beta-

and gamma cellulose when pulp is treated in the standard manner with 17.5% NaOH solution. A cooking or bleaching treatment which is too drastic causes a chemical degradation which gives an inferior pulp deficient in such physical properties as strength and opacity. This degradation is clearly shown by an increase in the percentage of alkali soluble material. The test is particularly sensitive to degradation resulting from the bleaching operation and the percentage soluble will show an increase before any serious loss of physical properties is apparent. When the pulp has been overbleached enough to show a marked effect on its physical properties the amount of soluble material will show a marked increase often amounting to 50% of the original solubility. Thus this test is a valuable control test to detect when the cooking or bleaching processes are too drastic. This method is standardized as TAPPI T 212 m 54.

**Apparatus**—The water bath employed in this determination must be so designed as to ensure that the temperature of the material during treatment is uniformly maintained at 97 to 100°C. When a new bath is used the temperature of the material during the treatment should be rechecked. The type of bath recommended is one which is covered and has holes in the top large enough so that beakers may be set down into the bath until they are supported by the flared rim. The top of the beaker should be nearly level with the cover of the bath. The sides of the beaker are entirely surrounded by boiling water or steam when this type of bath is used. The height of the water in the bath should be maintained at a level above that of the liquid in the beakers.

Tall form 200 ml Pyrex beakers should be used. Fritted glass crucibles (porosity 3) are recommended for filtering the treated pulp although alundum crucibles of a similar porosity are also suitable.

**Reagent Caustic Soda Solution** The 1% NaOH solution (0.25 normal) is made by dissolving 10 g of solid NaOH in water and diluting to 1 liter. Determine the NaOH content by titrating with standard acid first using phenolphthalein as an indicator then continuing the titration using methyl orange indicator. The difference between the volume used for the phenolphthalein end point and that used for the methyl orange end point represents that consumed by half the  $\text{Na}_2\text{CO}_3$  present. By subtracting this difference from the volume used for the phenolphthalein end point the volume required to neutralize the NaOH is obtained and from this volume the NaOH concentration is calculated. This shall then be adjusted to between 0.9 and 1.1%.

**Test Sample**—A sample which is representative of the pulp being tested shall be air dried and placed in an air tight container. The moisture content shall be determined by TAPPI Standard 210 m (p 1761). If the pulp is in the form of machine dried or pressed sheets which do not absorb liquid readily it should first be disintegrated to slush form in water then filtered into pads which are dried without any pressing. In this way the pulp is obtained in a form which readily disintegrates in the alkali solution.

**Procedure**—Accurately weigh on an analytical balance two samples of the air dried pulp each equal to  $2 \pm 0.1$  g of moisture free pulp. To each sample in a tall form 200 ml beaker add 100 ml of 1% NaOH solution measured with a pipette. Stir the pulp until it is completely disintegrated cover the beakers with watch glasses and place in the water bath which must be boiling steadily. Leave the beakers in the bath for exactly 1 hour. Stir the contents three times at 10, 15 and 25 minutes after the beakers are placed in the bath. At the end of the 1 hour

period, filter the contents of each beaker by suction on a tared crucible. First wash the pulp briefly with hot water, then with 50 ml. of 10% acetic acid, and then wash thoroughly with hot water. Dry the crucible and contents at  $105 \pm 3^\circ\text{C}$ ., cool in a desiccator, and weigh in a stoppered weighing bottle. Calculate the loss in weight of the moisture-free sample.

**Report.**—The result shall be reported as percentage of the moisture-free weight soluble in the NaOH solution. This value may be corrected, if desired, for hot-water solubility by subtracting from it the percentage of the moisture-free material soluble in hot water as determined by TAPPI Standard T 207 m (p. 1760). In this case the result shall be reported as “corrected.”

**Precision.**—The results of duplicate tests should not vary by more than 5% of the average result, and by careful work the deviation can be kept below 2%. The results are usually somewhat higher than those obtained by the method previously used because with the old method of heating, the temperature of the material during treatment was often below  $90^\circ\text{C}$ .

### PERMANGANATE NUMBER OF PULP <sup>43</sup>

This method is adapted to the determination of the relative “hardness” or bleachability of pulp. It may be used upon all ordinary types and grades of chemical wood pulp (sulfite, soda, or sulfate) sampled in any condition of dryness and at any stage of processing.

The permanganate number is, by definition, the number of milliliters of tenth normal potassium permanganate solution (0.1 *N*  $\text{KMnO}_4$ ) absorbed by 1 g. of moisture-free pulp under certain specified and carefully controlled conditions. This method is standardized as TAPPI T 214 m-50.

**Apparatus.** Mechanical Stirrer.—With a propeller-type agitator made of glass or other noncorrosive material. A propeller speed of  $500 \pm 100$  r.p.m. with an agitator 1 in. in diameter is recommended.

**Reaction Beakers.**—One or more 1000- or 1500-ml. white porcelain or white enamel-lined reaction beakers. Glass beakers of the same sizes may be used, but white-lined beakers are especially suitable for the titration in this method.

**Two Burets.**—Preferably of 50-ml. capacity and graduated to 0.1 ml.

**Stopwatch or Timing Clock.**

**Funnel and Filter Flask.**—A small Büchner funnel and filter flask when slush pulps are being tested.

**Reagents.** Potassium Permanganate Solution, 0.1 *N*.—Of exact or known strength, accurate to  $\pm 0.0005$  *N*  $\text{KMnO}_4$ .

Sodium Thiosulfate Solution, 0.1 *N*.—Of exact or known strength, accurate to  $\pm 0.0005$  *N*  $\text{Na}_2\text{S}_2\text{O}_3$ .

Potassium Iodide Solution.—Approximately normal, 166 g. of KI per liter. The solution should not contain free iodine or iodate. The latter, if present, will liberate free iodine upon acidification of the solution.

Sulfuric Acid, approximately 4 *N*. Add 112 ml. of c.p. concentrated  $\text{H}_2\text{SO}_4$  (94.5 to 96.5%) to about 500 ml. of cold water and dilute to 1 liter at  $20^\circ\text{C}$ .

Starch Indicator Solution.—Triturate 5 g. of arrowroot starch with a little cold water and then add, with constant stirring, 1000 ml. of boiling water. Set aside

<sup>43</sup> Wiles, R. H., Paper Trade J., 98, 34–35, March 15, 1934.

to cool and then decant or filter. Add 2 ml of oil of cassia or chloroform as a preservative.

**NOTE**—With some starches boiling the suspension for 1 minute and then cooling rapidly has been found to increase the sharpness of the end point.

Do not use so called soluble starch for this purpose unless it passes the following test: 5 ml of the soluble starch solution prepared as above should give a deep blue color when added to 100 ml of water containing 0.05 ml of 1% iodine and should become colorless with the subsequent addition of 0.05 ml of 0.1 N sodium thiosulfate.

Thyodene, an indicator used in powder form gives a sharper end point than most starches and keeps indefinitely.

**Test Specimen**—The test specimen shall consist of  $1 \pm 0.02$  g of moisture free pulp accurately determined to the nearest 0.005 g. It shall be representative of the whole flow or lot of pulp sampled.

While any convenient and suitable method may be used to weigh or to measure out the portion of the pulp sample used as the test specimen sufficient accuracy in weight usually cannot be obtained unless the moisture content of the sample is accurately determined on a separate portion and a quantity equivalent to 100 g of dry pulp weighed or measured out.

The following are examples of suitable methods of obtaining the test specimens:

1. If the pulp is sampled as slush or from wet laps dilute a portion containing from about 5 to 30 g of dry pulp to about 0.2% consistency with pure water. While stirring vigorously remove a volume equivalent to 1 or 2 g. Accurately measure the volume in a graduated cylinder or weigh in a tared beaker to  $\pm 0.5$  g then filter in a Buchner funnel using a filter paper which has previously been dried and weighed and dry in an oven at 100 to 105°C to determine the actual moisture free weight of pulp in that volume. Calculate the volume required to contain 100 g of moisture free pulp. Measure out this portion after vigorous stirring to constitute the test specimen.

2. If the pulp is sampled from dry laps or from wet laps which have been air dried shred the portions mix together determine the moisture content on a portion of the mixture then weigh out a quantity equal to 100 g of moisture free pulp. Disintegrate it for convenience in the reaction beaker with about 50 ml of water if a glass rod is used for disintegration or if a high speed stirrer is available use about 400 ml of water.

**Procedure**—Always adjust the reaction mixture at the commencement of the test to  $0.00333 \pm 0.0001$  N in  $\text{KMnO}_4$  and  $0.133 \pm 0.005$  N in  $\text{H}_2\text{SO}_4$  equal volumes of 0.1 N  $\text{KMnO}_4$  and 4 N  $\text{H}_2\text{SO}_4$  being diluted with the required amount of water to give this concentration. This is accomplished as follows:

For pulps containing little lignin and which have a permanganate number not greater than 20 use 25.0 ml of 0.1 N  $\text{KMnO}_4$ ,  $25 \pm 1$  ml of 4 N  $\text{H}_2\text{SO}_4$  and 700 ml of water (including any with the pulp specimen) to give a total volume of 750 ml. For pulps of high lignin content and which have a permanganate number greater than 20 when 25 ml of  $\text{KMnO}_4$  are employed use 40 ml of 0.1 N  $\text{KMnO}_4$ ,  $40 \pm 1$  ml of 4 N  $\text{H}_2\text{SO}_4$  and 1120 ml of water to give a total volume of 1200 ml. If the observed permanganate number is above 35, the results should be reported as over 35 or an increased volume of  $\text{KMnO}_4$  should be used and the conditions employed for the determination stated.

If because of exceptional circumstances it is necessary to use quantities of  $\text{KMnO}_4$  other than those given above report the actual volume used. In all cases, however, use the same volume of 4 N  $\text{H}_2\text{SO}_4$  as of 0.1 N  $\text{KMnO}_4$  and add the

necessary quantity of distilled water required to dilute the mixture to  $N/300$  in  $\text{KMnO}_4$ .

Accurately measure the desired amount of  $0.1\ N\ \text{KMnO}_4$  into a small beaker. Measure a like amount of  $4\ N\ \text{H}_2\text{SO}_4$  into another beaker of suitable size or into a graduated cylinder. Calculate the quantity of water which will be required to dilute the mixture to  $N/300$  in  $\text{KMnO}_4$  and add this amount, less the volume in which the test specimen is suspended, to the vessel containing the  $\text{H}_2\text{SO}_4$ . Adjust the temperature, if necessary, so that the mixture of all components will be at  $25 \pm 1^\circ\text{C}$ . In locations where the temperature of the contents might vary from the prescribed limits, a constant-temperature bath is recommended for holding the beaker during the reaction period. Place the pulp specimen in the reaction beaker under the stirrer and add the  $\text{H}_2\text{SO}_4$ -water mixture to it, reserving a few milliliters of the mixture for rinsing out the permanganate beaker. Start the stirrer and quickly add the measured amount of  $\text{KMnO}_4$ . Start the stopwatch, then quickly rinse the beaker and add to the reaction mixture.

Allow the reaction to continue for 5 minutes  $\pm$  10 seconds from the time the  $\text{KMnO}_4$  was added. Then stop the reaction by adding 5 ml. of KI solution to the mixture and stop the stirrer.

NOTE.—If desired, the  $\text{KMnO}_4$  may be added directly to the acidified pulp suspension by means of a calibrated pipet having a delivery time of less than 20 seconds. The effective reaction time of 5 minutes  $\pm$  10 seconds should then be measured from the middle of the pipet delivery period.

The excess  $\text{KMnO}_4$  is immediately reacted upon by the KI when the latter is added, releasing free iodine equivalent to the amount of  $\text{KMnO}_4$  remaining. Titrate this free I with the  $0.1\ N\ \text{Na}_2\text{S}_2\text{O}_3$  solution in the reaction beaker without filtering out the fibers, adding a few drops of starch indicator near the end of the titration.

Subtract the number of milliliters of  $0.1\ N\ \text{Na}_2\text{S}_2\text{O}_3$  used in the back-titration from the number of milliliters of  $0.1\ N\ \text{KMnO}_4$  originally added to the mixture and divide the difference by the moisture-free weight of the test specimen to obtain the permanganate number.

Report.—Report to the nearest 0.1 ml. the number of milliliters of  $0.1\ N\ \text{KMnO}_4$  consumed by 1 g. of moisture-free pulp as the permanganate number.

Precision.—Complete duplicate tests, including sampling, are expected to agree within 0.5. Duplicate tests on a single sample should agree within 0.1.

**Additional Information.** Conversion to Equivalent Bleach Consumption.—When this test is used for sulfite pulps, the equivalent bleach consumption, i.e., the grams of Cl absorbed per 100 g. of moisture-free pulp, may be calculated. The permanganate number as determined is multiplied by 0.355 and the product is divided by a factor (Table 38-4). The number obtained is about the number of grams of Cl in the form of calcium hypochlorite solution necessary to bleach 100 g. of dry pulp in a single-stage operation. This number again multiplied by 2.86 gives the same information in terms of percentage of 35% bleaching powder. The exact conversion factors depend upon the character of the pulp and upon the particular type of bleaching process used—for example, alkaline pulps usually require higher factors than those for sulfite pulp which are given in Table 38-4. For accurate conversion it is necessary to obtain the factors experimentally.

Approximate conversion is possible between this permanganate number and the figures obtained by various other permanganate, chlorine, and bleach-consumption

TABLE 38 4 APPROXIMATE CONVERSION OF PERMANGANATE NUMBER TO EQUIVALENT BLEACH CONSUMPTION (Applicable to Sulfite Pulp)

<i>Perman- ganate Number</i>	<i>Factor</i>	<i>Percentage Bleach Con- sumption as Chlorine</i>	<i>Perman- ganate Number</i>	<i>Factor</i>	<i>Percentage Bleach Con- sumpt on as Chlorine</i>
1	0 818	0 43	21	0 664	11 21
2	0 810	0 88	22	0 656	11 90
3	0 802	1 33	23	0 648	12 60
4	0 794	1 79	24	0 641	13 27
5	0 786	2 26	25	0 634	14 00
6	0 778	2 74	26	0 626	14 73
7	0 770	3 23	27	0 618	15 50
8	0 762	3 72	28	0 611	16 25
9	0 755	4 24	29	0 604	17 05
10	0 747	4 75	30	0 596	17 85
11	0 739	5 29	31	0 589	18 70
12	0 732	5 82	32	0 582	19 50
13	0 724	6 39	33	0 574	20 40
14	0 716	6 94	34	0 567	21 25
15	0 709	7 52	35	0 560	22 15
16	0 702	8 10	36	0 552	23 10
17	0 694	8 70	37	0 545	24 10
18	0 686	9 31	38	0 538	25 05
19	0 679	9 94	39	0 531	26 05
20	0 672	10 56	40	0 522	27 20

$$\text{Percentage bleach consumption as chlorine} = \frac{\text{Permanganate number} \times 0.355}{\text{Factor}}$$

methods frequently used in the industry. Exact conversion can be reliably obtained only when the two or more methods in question are applied to pulp of very similar character as to species source of wood and nature of the pulping and other treatments.

## COPPER NUMBER OF PULP

### TAPPI METHOD

This method is suitable for all pulps although its principal use is in the evaluation of pulps free from unbleached groundwood or other highly lignified fibers. This method is standardized as TAPPI T 215 m 50.

**Apparatus**—The special apparatus required for this test is (1) a grinder which will completely disintegrate the pulp without heating or contaminating it and (2) a steam or oil bath which can be maintained at 100°C. The grinder shall be a Koerner type or its equivalent.

**Reagents** **Copper Sulfate Solution**—Dissolve 100 g of copper sulfate ( $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ ) in water and dilute to 1 liter.

**Carbonate Bicarbonate Solution**—Dissolve 350 g of sodium carbonate crystals



( $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$ ) or 129 g. of anhydrous  $\text{Na}_2\text{CO}_3$ , and 50 g. of sodium bicarbonate ( $\text{NaHCO}_3$ ) in water and dilute to 1 liter.

**Molybdophosphoric Acid.**—Dissolve 100 g. of sodium molybdate ( $\text{Na}_2\text{MoO}_4 \cdot \text{H}_2\text{O}$ ) and 75 ml. of phosphoric acid (83%) in a mixture of 275 ml. of concentrated  $\text{H}_2\text{SO}_4$  and 1.75 l. of water.

**Sodium Carbonate Solution.**—An approximately 5% solution of  $\text{Na}_2\text{CO}_3$  in water.

**0.05 N Potassium Permanganate Solution.**—1.5815 g. of  $\text{KMnO}_4$  per liter.

**Test Specimen.**—The specimen for test shall be cut from the test sample in such a way as to be thoroughly representative of it, and shall be completely disintegrated in the grinder.

**Procedure.**—Allow the specimen to come to moisture equilibrium with the atmosphere of the balance. Weigh about 1.5 g. (to nearest 10 mg.) of the ground pulp. Weigh at the same time samples for moisture and ash determinations which shall be made by standard methods.

Immediately before use add 5.0 ml. of copper sulfate solution to 95 ml. of carbonate-bicarbonate solution. Bring the mixture to a boil in 2 minutes and pour it over 1.5 g. of the ground sample in a 125-ml. Erlenmeyer flask. Stir well with a glass rod in order to distribute the fibers and to remove air bubbles. Fit the flask with a loosely fitting glass bulb or stopper and submerge completely in a steam bath at atmospheric pressure. Occasionally fibers tend to float to the surface; therefore, the flask should be shaken from time to time to redistribute them. Remove the flask from the steam bath at the end of 3 hours. Filter on an ashless filter paper in a 7.5 cm. Büchner funnel, using suction. Wash by flooding with 100 ml. of 5%  $\text{Na}_2\text{CO}_3$  solution at about  $20^\circ\text{C}$ . and then by flooding with 250 ml. of hot water (about  $95^\circ\text{C}$ .), discarding the filtrates. Transfer the fibers and filter paper to a small beaker, add 25 ml. of molybdophosphoric acid and macerate well with a flattened glass rod. Transfer to a Büchner funnel again and wash thoroughly with cold water until the blue molybdenum color is removed from the fibers. Dilute the filtrate with water to approximately 700 ml. and titrate it with 0.05 N  $\text{KMnO}_4$  to a faint pink.

**NOTE.**—The amount of copper sulfate solution given above is sufficient for a copper number not greater than approximately 6, and this figure is seldom exceeded except in pulps containing highly lignified fibers such as groundwood, or in pulps which have deteriorated considerably. If the copper number exceeds 6, increase the amount of this solution to 10 ml. and the amount of molybdophosphoric acid to 50 ml., or as much as may be necessary, retaining the ratio between the solutions.

**Calculation.**—The copper number is defined as the number of grams of metallic Cu in the  $\text{Cu}_2\text{O}$  resulting from the reduction of the  $\text{CuSO}_4$  by 100 g. of the pulp fibers. This is calculated by the formula

$$\text{Copper number} = \frac{6.36 \times \text{ml. KMnO}_4 \times N}{W},$$

where  $N$  is the normality of the  $\text{KMnO}_4$  and  $W$  is the weight in grams of the test specimen after deduction of the weight of the nonfibrous materials. Correction of the weight of the test specimen shall always be made for moisture and ash. Correction for other nonfibrous components shall be made whenever they are present in significant amounts. Not less than two determinations shall be made, and the average of the results, rounded off to the nearest 0.1, shall be reported. Duplicate determinations should agree within 0.2.

**Report**—The copper number shall be reported to one decimal place on the basis of total fiber content

**Additional Information**—This method is essentially the Braidy<sup>44</sup> modification of the original Schwalbe<sup>45</sup> method with modifications for its adaptation to paper proposed by Scribner and Brode<sup>46</sup> and by Burton and Rasch<sup>47</sup>

This method has been adopted as part of the official Swedish method CCA3 by the Analysis Committee of the Central Laboratory of the Cellulose Industry<sup>48</sup>. The Swedish method includes also as an alternative procedure the Hagglund method which is described below. The latter is much quicker and is suitable for routine control but results are somewhat different from those obtained by this method

### HAGGLUND METHOD

**Reagents** **Copper Sulfate Solution**—Dissolve 60 g of  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  in water and dilute to 1 liter

**Tartrate Solution**—Dissolve 200 g of sodium potassium tartrate ( $\text{NaKC}_4\text{H}_4\text{O}_6$ ) and 100 g of NaOH in water and dilute to 1 liter

**Ferric Sulfate Solution**—Dissolve 50 g of anhydrous  $\text{Fe}(\text{SO}_4)_3$  in 200 g (109 ml) of concentrated  $\text{H}_2\text{SO}_4$  (sp gr 1.84) and dilute with water to 1 liter. Before using the solution add 0.1 N  $\text{KMnO}_4$  drop by drop until the color after stirring is faintly pink

**Potassium Permanganate Solution** 0.1 N accurately standardized

**Procedure**—Weigh about 1 g (to the nearest 10 mg) of the pulp sample of known moisture content and place in a 150 ml beaker. Heat to boiling a mixture of 20 ml of copper sulfate solution and 20 ml of tartrate solution. Add the boiling mixture to the pulp and boil vigorously for exactly 5 minutes timed with a stop watch. Filter through an 8 cm Buchner funnel on an ashless filter paper and wash with 500 ml of hot distilled water (at about 90°C) and then with 250 ml of cool water. Discard the filtrate.

Transfer the filter paper containing the pulp to the original beaker which has been washed out and add 25 ml of the ferric sulfate solution. Stir with a glass rod and again filter on a new filter paper collecting the filtrate in a clean suction flask. Wash the pulp on the filter first with 25 ml of ferric sulfate solution and then with 500 ml of distilled water. Titrate the filtrate with 0.1 N  $\text{KMnO}_4$  to a faint pink color and calculate the copper number of the pulp. Results should be reported as Hagglund copper number

### PENTOSANS IN PULP<sup>49, 50, 51</sup>

By this method a specimen of the pulp is treated with hot hydrochloric acid (12%) to hydrolyze the pentosans to pentoses which are then dehydrated to furfural

<sup>44</sup> Clibbens D. and Geake A. J. *Text Inst.* 15, T31 1924

<sup>45</sup> Schwalbe C. *Die Chemie der Cellulose* p. 625 1912

<sup>46</sup> Scribner B. W. and Brode W. R. *Technologic Paper* No. 354 National Bureau of Standards

<sup>47</sup> Burton J. O. and Rasch R. H. J. *Research Natl. Bureau Standards* R1 293 April 1934. Includes an illustrated description of the Koerner type of grinder

<sup>48</sup> Svensk Papperstidning 46 528 Nov. 30 1943. See also *Papper Fabr. Verkblatt* Nr. 8 1 1935

<sup>49</sup> Johanson Axel *Svensk Papperstidning* 55, 820-28 Nov. 15 1952 (Article in English)

<sup>50</sup> Hughes C. E. and Acree S. F. J. *Research NBS* 21, 329 1938

<sup>51</sup> Tunissen Pieter H. *Anal. Chem.* 21, C20 1919

The furfural is distilled, collected, and analyzed by one of two methods. If the sample contains less than 10% pentosans, an aliquot of the distillate is treated with aniline acetate,<sup>52, 53</sup> and the color allowed to develop. The transmittance of the solution is measured at 520  $m\mu$ , and the furfural determined from a graph of readings of solutions containing known amounts. If the sample contains 10% or more of pentosans, the furfural in the distillate is determined by a volumetric bromination procedure. This method is standardized as TAPPI T 223 m-58.

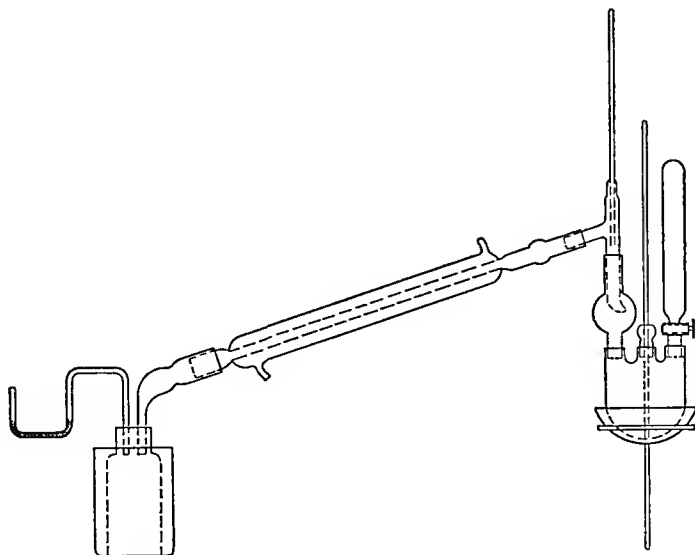


FIG. 38-15. Pentosan Distillation Apparatus.

**Apparatus.** Distillation Apparatus.—Consisting of a 500-ml. standard taper 24/40 two-neck round-bottom flask, or a three-neck flask as shown in Fig. 38-15, with the center opening closed by a stopper firmly wired in place. The flask is heated either with a heating mantle controlled by a variable transformer, or with a gas burner. One opening of the flask contains a 500-ml. standard-taper 24/40 dropping funnel graduated at 50-ml. intervals; the other contains a three-way, 75° connecting tube, with two standard-taper 24/40 interjoints to fit both the round-bottom flask and a suitable condenser, and also with a standard-taper 10/30 opening at the top, in which a thermometer, covering the range 100 to 120°C., may be placed if desired. To the lower end of the condenser is fitted an adapter with its lower end drawn out so that it will pass through one hole of a two-hole rubber stopper in the mouth of a 500- or 1000-ml. receiving bottle or flask, standing in an ice bath. The larger size is desirable for the volumetric method. Through the other hole of the stopper passes a U-shaped trap containing a few beads and a little water.

Standard-taper glassware rather than glass tubing and rubber stoppers should be used for the distilling flask so as not to restrict the flow of vapor from the flask into the condenser.

<sup>52</sup> Adams, G. A., and Castagne, A. E., Can. J. Research, Sec. B, 26, 314, March, 1948.

<sup>53</sup> Stillings, R. A., and Browning, B. L., Ind. Eng. Chem., Anal. Ed., 12, 499, Sept., 1940.

Starch Solution, 5% (or Thiodene).

**Test Specimen.**—Obtain a representative sample weighing at least 4 g. so that there is enough for a duplicate determination. Reduce the sample to an open fluffly form by tearing apart by hand; then thoroughly mix.

**Procedure. Distillation.**—Allow the sample to come to moisture equilibrium with the atmosphere. Weigh to the nearest milligram a 1-g. test specimen and at the same time a specimen for a moisture determination.

NOTE.—If pentosans are to be determined colorimetrically: for an expected pentosan content of 2% or less, weigh out a 1-g. specimen; for an expected pentosan content of 2 to 10% or over, reduce the weight of the specimen approximately in proportion.

Place the specimen in the distilling flask and add 100 ml. of diluted HCl, washing all the fibers to the bottom. Mark the flask to indicate the liquid level. Place a few beads in the flask and insert the distilling head and dropping funnel. Add 300 ml. of diluted HCl to the dropping funnel.

Place the distillate receiver in an ice bath to prevent the escape of furfural and add a little distilled water to the trap. Heat the distilling flask.

Distill for 90 minutes from the beginning of the distillation at a rate of approximately 50 ml. every 15 minutes, and collect 300 ml. of the distillate in the receiving flask in that time. (The temperature of the vapor should be 105 to 110°C.) While distillation is proceeding, adjust the stopcock in the dropping funnel so that acid is added at such a rate as to maintain the original 100 ml. level in the flask.

After distillation, use the Colorimetric Method if the expected pentosan content is less than 10%, and the Volumetric Method if the expected pentosan content is 10% or more.

**Colorimetric Determination of Pentosans. Calibration of Colorimeter.**—Weigh  $0.500 \pm 0.001$  g. of pure furfural from a weighing bottle into a 1-liter volumetric flask, and dilute to the mark at 20°C. Pipet volumes of 1, 2, 5, 10, 15, 20, 25, and 30 ml. of this solution into separate 1-liter volumetric flasks at 20°C. and dilute with NaCl solution to obtain solutions containing 0.5, 1.0, 2.5, 5.0, 7.5, 10.0, 12.5, and 15.0 mg. of furfural per liter.

Pipet 20-ml. aliquots of these prepared solutions into the 100-ml. stoppered volumetric flasks. Prepare a blank using 25 ml. NaCl solution without furfural. Adjust the solutions to  $20 \pm 1^\circ\text{C}$ . Add 20 ml. of the stabilizer solution to each flask and pipet into each, at 5-minute intervals, 50 ml. of the freshly prepared aniline acetate reagent.

NOTE.—The aniline acetate reagent is added to the flasks at successive 5-minute intervals so as to measure the transmittance of each solution after a reaction time of exactly 30 minutes.

Dilute to the 100-ml. mark with water at 20°C., stopper, and mix well by shaking each flask a minimum of 25 times.

Place the solutions in a bath at  $20 \pm 1^\circ\text{C}$ ., let each stand for 30 minutes from the time the aniline acetate reagent was added, then measure the transmittance of each at 520  $\mu$ . On semilog paper plot the percentage transmittance against the weight of furfural in milligrams. The actual weights in each of the 100-ml. flasks are 0.01, 0.02, 0.05, 0.10, 0.15, 0.20, 0.25, and 0.30 mg., respectively.

NOTE—The calibration curve should be spot checked occasionally prior to using because of possible changes in the characteristics of the photometer.

*Pentosans in Distillate from Specimen*—During the distillation period adjust the other reagents and distilled water to a temperature of  $20 \pm 1^\circ\text{C}$ .

When distillation is complete remove the stopper from the receiver and, with a stream of water from the wash bottle, wash the contents of the trap and the adapter into it. Transfer the contents of the receiver to a 1 liter volumetric flask rinsing out the receiver into the flask with a couple of small portions of water. Dilute the distillate and rinsings to the 1 liter mark at  $20^\circ\text{C}$  and mix well. With a pipet transfer to a 100 ml beaker a 20 ml or other aliquot. Add 1 drop of phenolphthalein and neutralize with 24% NaOH solution from the 10 ml Mohr pipet or buret with the bead valve. Record the volume to the nearest 0.1 ml.

NOTE—Adjust the size of the aliquot to the pentosan content of the pulp sample and the cell length of the colorimeter.

Pipet a second 20 ml (or other) aliquot to a 100 ml volumetric flask having a low actinic transmission. Add the same volume of sodium hydroxide solution found necessary to neutralize its acidity and in addition 20 ml of the stabilizer solution measured in a graduate. Place the flask in the water bath at  $20 \pm 1^\circ\text{C}$ . Prepare a blank by adding 25 ml of NaCl solution and 20 ml of the stabilizer solution to another 100 ml low actinic volumetric flask and place it in the bath.

NOTE—If dark flasks are not available for this purpose protect the solutions from strong light.

Pipet 50 ml of the freshly made aniline acetate reagent to the flask containing a specimen. Dilute each solution to the mark with water, stopper and mix well. Allow the solutions to stand at  $20^\circ\text{C}$  for  $30 \pm 2$  minutes to allow the color to develop. At the end of 30 minutes, set the instrument at 100% transmittance with the blank in the usual way, then in turn transfer each of the specimen solutions to the cell after having first rinsed the cell with the solution. Measure and record the transmittance.

NOTE—Other volatile substances such as hydroxymethylfurfural have a negligible effect on the transmittance.

*Calculations*—The ratio  $\text{C}_5\text{H}_8\text{O}_4/\text{C}_5\text{H}_4\text{O}_2$  expresses the theoretical ratio of pentosan to furfural. This theoretical ratio is numerically  $132/96 = 1.38$  but an empirical factor of 1.56 or 1.58<sup>54</sup> should be used instead giving a furfural yield of  $(1.38/1.58) \times 100$ , 87.5% of the theoretical yield. Correcting for incomplete conversion, the formula becomes

$$\begin{aligned} \text{Percentage pentosans} &= \frac{\text{mg furfural found from the curve} \times 1.58 \times 50 \times 100}{1000 \times \text{wt of air-dry specimen in grams}} \\ &= \frac{7.9 \times \text{mg furfural}}{\text{wt specimen} (100 - \% \text{H}_2\text{O})/100} \end{aligned}$$

<sup>54</sup> Laitner, H. F., and Wilson, W. K. J. Research. NBS 22, 471, Apr., 1939.

*Example.*—Moisture in the conditioned sample, previously determined = 4.86%.

Specimen weight = 1.005 grams

Transmittance = 71.4

Milligrams of furfural from curve = 0.086

$$\text{Pentosans} = \frac{7.9 \times 0.086}{1.005 \times (100 - 4.86)/100} = 0.71\%$$

**Volumetric Determination of Pentosans.**—Transfer the condensate, including that in the trap, to the 1-liter glass-stoppered flask or bottle and add 50 ml., less the volume of liquid in the trap, of water. Add 250 g. of the crushed special ice. After the temperature of the mixture has fallen to 0°C. or lower, gently add 20 ml. of 0.2 *N* bromate-bromide from a pipet with minimum agitation, close the flask or bottle promptly with its ground-glass stopper, shake well, and let stand for exactly 5 minutes. The temperature should still be 0°C. or lower. Remove the stopper, add 10 ml. of 10% KI solution from a small graduate, and replace the stopper as quickly as possible. Shake the mixture thoroughly to allow absorption of the bromine vapor, then titrate with 0.1 *N* thiosulfate until colorless, using starch indicator toward the end of the titration.

Make a blank titration in exactly the same manner, using all reagents, including the ice, except starting with 270 ml. of 3.5 *N* HCl, diluted to 350 ml., instead of 300 ml. of condensate plus 50 ml. of water.

*Calculations.*

$$\text{Pentosans} = \left( \frac{7.58N(V_2 - V_1)}{W} \right) - 1.1\%$$

where *N* = normality of the thiosulfate solution

*V*<sub>1</sub> = volume of thiosulfate solution used in the test

*V*<sub>2</sub> = volume of thiosulfate solution used in the blank

*W* = weight of the moisture-free specimen.

The factor 7.58 is the product of 0.048 × 1.58 × 100, where 0.048 is the weight of furfural in grams corresponding to 1 ml. of *N* thiosulfate, and 1.58 is an empirical factor for converting furfural to pentosans: 1.1 is subtracted to compensate for the hydroxymethylfurfural normally found in wood cellulose.<sup>55</sup> For cotton cellulose, the figure is very small: 0.2.

**Report.**—Report the pentosans as a percentage of the moisture-free pulp to the nearest 0.1%. Single determinations may be satisfactory for routine samples, but make duplicate determinations for special samples. If duplicate tests do not agree to within 5% of each other or to within 0.1%, repeat the determination.

<sup>55</sup> Adams, G. A., and Castagne, A. E., *Can. J. Research, Sec. B*, 26, 314, March, 1948.

volume of 500 ml., to a 1-liter tooled neck bottle (see Fig. 38-16) equipped with a rubber stopper carrying two glass tubes, of which one (*A*) is straight and extends to within approximately 5 cm. of the bottom of the bottle, and the other has two right-angle bends (*B* and *C*) and extends just through the rubber stopper. One of the side tubes (*B* or *C*) is connected to a suction source and the other to the nitrogen supply.

Wire down the rubber stopper, exhaust the air with a laboratory water pump, and refill the bottle with nitrogen at 2 pounds pressure three separate times. The rubber tubes and pinch clamps attached to the glass tubes of the solution bottle, as shown in Fig. 38-16, are used for this purpose. Draw a partial vacuum on the bottle and add 160 ml. of 70% ethylenediamine, taking care that no air enters the bottle. This is accomplished by inserting a funnel in the rubber tube attached to the longer glass tube of the solution bottle and opening the pinch clamp just enough to allow the ethylenediamine to be drawn into the bottle. Since considerable heat is evolved at this point, it is desirable to keep cold water running over the bottle during the initial phase of the reaction. After the addition of the ethylenediamine, the gas over the liquid should be alternately evacuated and flushed three times with nitrogen at 2 pounds pressure.

With the pinchcocks closed, place the bottle and contents on a rotary shaker travelling from 5 to 10 r.p.m. and rotate for 12 to 16 hours. Then remove the bottle and allow to stand for at least 8 hours to thoroughly settle the excess  $\text{Cu}(\text{OH})_2$  sludge.

If a rotary shaker is not available, shake the contents of the bottle several times during the course of an hour, and then let stand 12 to 16 hours. A clear supernatant liquor will usually be obtained, but if desired, the solution may be filtered through a Type C Corning fritted-glass Büchner funnel, using suction, and again stored under nitrogen.

**Standardization of  $\text{Cu}(\text{En})_2$  Solution.—Copper.** Remove a 25-ml. sample of the clear liquor by means of a pipet and dilute to 250 ml. in a volumetric flask. Pipet out a 25-ml. aliquot, add approximately 3 g. of KI, acidify with 50 ml. of 4 *N*  $\text{H}_2\text{SO}_4$ , and titrate with 0.1 *N* thiosulfate solution to the starch end point. Add 10 ml. of 20%  $\text{NH}_4\text{CNS}$  solution just before the end point is reached, to intensify it. Multiply the milliliters of thiosulfate required by 0.04 to obtain the molarity of the original solution in copper.

**Ethylenediamine.** Take another 25-ml. aliquot of the diluted solution, add about 75 ml. of distilled water and 2 drops of methyl orange indicator, and titrate with standard 1.0 *N* acid solution to a faint pink coloration. The color change of the solution during the titration passes from dark blue to light blue to slate grey, and finally develops a pink tinge. Multiply the milliliters of 1.0 *N* acid required by 0.4 to obtain the alkalinity in hydrogen ion equivalents.

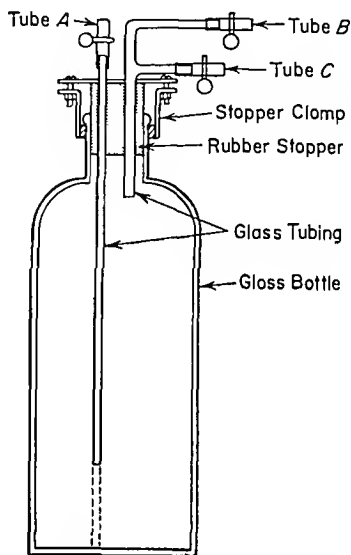


FIG. 38-16. Solution or Stock Bottle for  $\text{Cu}(\text{En})_2$  Viscosity Solvent.

**Calibration:** Standard-viscosity oil obtained from the National Bureau of Standards in the desired viscosity range is used for calibration.<sup>58</sup> When these pipets are calibrated with the standard oil and used in the recommended viscosity range, there is no appreciable kinetic energy correction necessary, and other viscometer errors such as loading, drainage, surface tension, etc., are negligible.

The pipet constant  $C$  is calculated from the formula:

$$C = \frac{V}{td}$$

where  $V$  = viscosity in centipoises,

$d$  = density of the solution,

$t$  = time in seconds for meniscus to pass between the two etched lines around capillary,

and  $C$  = pipet constant.

The constant  $C$  is determined with the use of standard-viscosity oil of known viscosity and density at 25°C. in the recommended range as follows:

Load the viscometer in an inverted vertical position with the capillary side submerged in the standard oil. Then apply suction to the other arm of the instrument and fill both small bulbs on the capillary arm with the oil. Bring the liquid into the working capillary to the etched mark. After filling the pipet, rotate it to its normal vertical position and place in a constant-temperature water bath held at  $25 \pm 0.1^\circ\text{C}$ . The liquid will drain into the lower reservoir during the time required for it to attain the bath temperature. When this temperature is reached (in approximately 5 minutes), determine the efflux time by drawing the liquid above the mark between the two bulbs and measuring the time required for the meniscus to pass from the mark between the two bulbs to the mark below the lower bulb. Run at least two determinations. The pipet constant is obtained by dividing the known viscosity of the oil by the product of its density and efflux time.

**Dissolving Tube.**—The glass dissolving tube used for dissolving the pulp samples is shown in Fig. 38-17. The stirrer consists of an electrolytic-copper rod approximately  $\frac{1}{8}$  in. in diameter, bent as shown in Fig. 38-17.

The dissolving tubes may be purchased from suppliers of scientific apparatus. Those made by the Scientific Glass Apparatus Company, Bloomfield, New Jersey, have been found satisfactory. The copper rod is conveniently made from No. 7 or No. 8 B. & S. gage copper wire after removing any insulation.

**Reagent. Cupriethylenediamine Solution.**—A solution 0.5  $M$  in copper is required.

**Procedure.**—Weigh out an amount of air-dry pulp equivalent to 0.125 g. of moisture-free pulp and place in the dissolving tube. (This is calculated by determining the moisture on a separate portion.) Then add 25 ml. of  $\text{Cu}(\text{En})_2$  (0.500  $M$

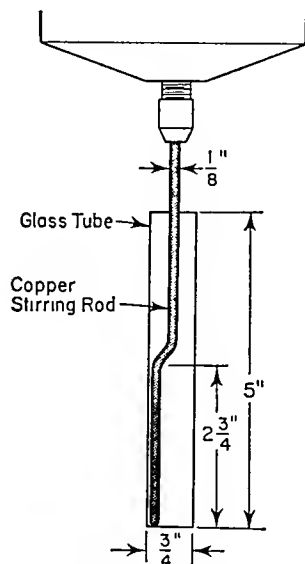


Fig. 38-17. Dissolving Tube.

<sup>58</sup> Calibrated viscosity pipets may be purchased from laboratory supply houses, if desired.



In determining the viscosity of an unknown  $\text{Cu(En)}_2$  cellulose solution, however, the equation is:

$$V' = Kt'(D - d'); \quad (2)$$

where  $V'$  = viscosity of unknown solution,

$t'$  = time of fall of aluminum ball through unknown solution,

and  $d'$  = density of  $\text{Cu(En)}_2$  cellulose solution at  $25.0^\circ\text{C.} = 1.052$ .

Then, from equation (1):

$$V' = \frac{V(D - 1.052)}{t(D - a)} t' = Ct'. \quad (3)$$

where  $\frac{V(D - 1.052)}{t(D - a)} = C$ , the tube constant for solutions of cellulose in  $\text{Cu(En)}_2$ .

**Reagents.** Cupriethylenediamine Solutions.—Two solutions are required: one  $0.167 \pm 0.003 M$  in copper, the other  $1.0 \pm 0.005 M$  in copper.

**Dissolving the Sample.**—When certain types of cellulose, especially those with a high viscosity, are dispersed in  $0.5 M \text{ Cu(En)}_2$ , there is a tendency toward surface gelatinization of the sample, leading to incomplete dispersion. To overcome this, it has been found desirable to wet the cellulose sample with the proper amount of weaker ( $0.167 M$ ) solution. The correct amount of the stronger ( $1.0 M$ ) solution is then added to bring the solvent to  $0.5$  copper molarity.

To determine the amount of each solution to be added, the following equations are used:

$$\frac{60W}{P} = \text{ml. of } 0.167 \text{ Cu(En)}_2 \text{ solution, and}$$

$$\frac{40W}{P} = \text{ml. of } 1.00 \text{ Cu(En)}_2 \text{ solution;}$$

where  $W$  = weight of moisture-free sample in grams,

and  $P$  = cellulose concentration in per cent.

It has been found that when the time of fall of the ball in a  $\text{Cu(En)}_2$  cellulose solution is less than 10 seconds or more than 30 to 40 seconds, the resulting viscosity may be in error. When the time of fall is 10 seconds or less, an error of 0.1 second in timing the falling ball will give an error in the viscosity figure of 1% or more. If the time of fall of one ball is much greater than 30 seconds, the total time required to obtain check results on two or more balls and to determine the temperature will be so great that temperature fluctuations may occur. Under such conditions the concentration of cellulose should be changed to more or less than 1% to keep the time of fall in a range greater than 10 seconds and less than 30 seconds. The following relationship between viscosity and time of fall for pulps of varying viscosities gives the approximate concentration at which pulps of such viscosities should be run:

Viscosity, Centipoises	Cellulose Concentration, Per cent	Moisture- Free Sample, Gram	Cupriethylenediamine	
			0.167 M, Ml	1.00 M, Ml
18 to 25	2.50	0.6250	15.00	10.00
25 to 45	2.00	5000	15.00	10.00
45 to 90	1.50	3750	15.00	10.00
70 to 150	1.25	3125	15.00	10.00
120 to 400	1.00	2500	15.00	10.00
350 to 1600	0.75	1875	15.00	10.00
1000 or more	0.60	1500	15.00	10.00

Make a preliminary determination on a 1% dispersion of the pulp sample in the  $\text{Cu}(\text{En})_2$  as described below under Procedure. Then from the above table select and weigh out the amount of sample necessary to give the proper cellulose concentration for the final determination.

**Procedure**—Connect the bottles containing the two  $\text{Cu}(\text{En})_2$  solutions to 25 ml side arm Mohr burets. Fill the burets by maintaining a 2 pound nitrogen pressure on the bottles. Add the calculated amount of 0.167 M solution to the dissolving bottle taking care that the pulp sample is thoroughly wetted. Then add the proper amount of the 1.00 M solution; sweep the bottle out with a stream of nitrogen for at least 15 seconds and quickly screw on the cap.

**Note**—The nitrogen is supplied through a vertical 5 mm glass tube the upper end of which is connected to a nitrogen cylinder with a reducing valve set at approximately 2 pounds per square inch pressure. The dissolving bottle is swept free of air by adjusting it to the glass tube in such a way that the lower end of the tube extends just below the neck; the bottle is then tipped and slowly rotated so that the nitrogen stream sweeps over the surface of the liquid at all corners of the bottle. The bottle cap should be held in such a position that the nitrogen escaping from the bottle will sweep out the interior of the cap.

Shake the solution bottle by hand or on a machine for exactly 3 minutes to disperse the cellulose completely. A convenient and satisfactory machine shaker maintains approximately 200 shaking cycles per minute with a 3 to 4 inch amplitude. At the end of this shaking time place the solution bottle on its side for 2 minutes to allow the large bubbles formed during shaking to escape. Then pour the solution carefully into the viscosity tube. (If this is done too rapidly, bubbles may be formed which will interfere with the accuracy of the test.)

Place the viscosity tube in a tube holder (Fig. 38-18) which is so constructed that the tube is held in a vertical position. Place a shielded fluorescent light behind the tube holder so that the passage of the ball can be seen. Measure to the nearest 0.1 second the time required for a  $\frac{1}{16}$  inch aluminum ball to fall between the etched rings on the tube. More than one ball should be timed to assure an accurate test. Duplicate times should agree within 1%.

As soon as the falling ball time has been determined, measure the temperature of the solution to the nearest 0.1°C. It is very important that the temperature of the room be relatively stable so that there will be no fluctuations in the solution temperature during the dropping of the balls and the temperature measurement.

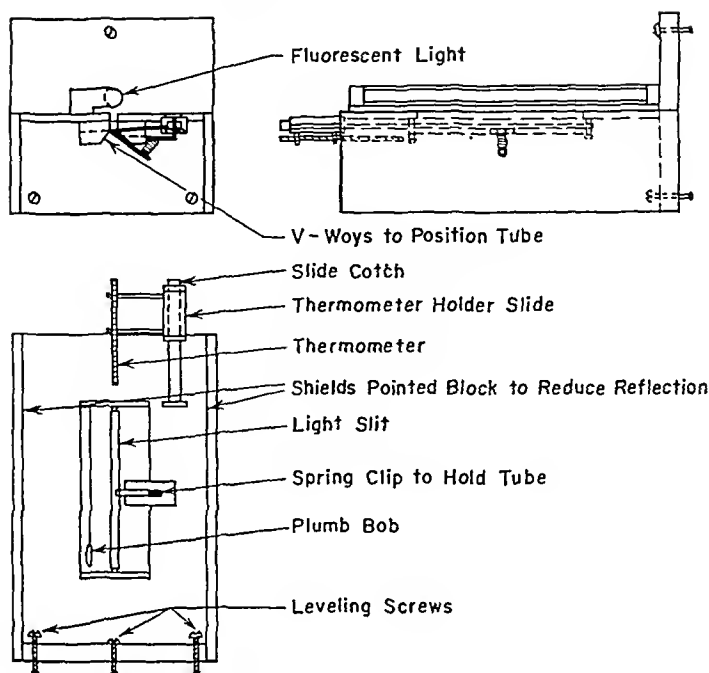


FIG. 38-18. Tube Holder.

**Calculation.**—The viscosity of the solution is calculated by the following equation:

$$\log V = \log C + \log t + (T - 25.0^\circ\text{C.})(0.01866),$$

where  $V$  = viscosity of  $\text{Cu}(\text{En})_2$  cellulose solution at  $25.0^\circ\text{C.}$ , in centipoises,

$t$  = time of fall in seconds,

$T$  = temperature of solution in degrees centigrade,

and  $C$  = tube constant.

If the time of fall is determined at concentrations other than 1%, make the temperature correction and apply the following formula to convert the viscosity determined at concentrations other than 1% to that of 1% cellulose concentration:

$$\log V_1 = \frac{\log V_p + (P - 1)(K)}{P},$$

where  $V_1$  = theoretical viscosity at 1% concentration and  $25.0^\circ\text{C.}$ , in centipoises,

$P$  = percentage concentration used,

$V_p$  = measured viscosity, at concentration  $P$  and  $25 \pm 0.1^\circ\text{C.}$ ,

and  $K$  = a constant which is 0.73 for bleached pulps and 0.63 for unbleached pulp.

**NOTE.**—For rag pulps the constant  $K$  is believed to be 0.73, although sufficient work has not been done as yet to establish this with certainty.

**Report.**—Results shall be reported in terms of centipoises as the cupriethylene-diamine viscosity by the falling-ball method and shall represent the average of at least two separate tests.

**Precision**—Duplicate samples should check within 2%

**Additional Information**—1 Unbleached pulps can be tested directly only by the falling ball method in the viscosity pipet method the undissolved lignin may plug the capillary For testing unbleached pulps by the viscosity pipet method and optionally by the falling ball method the following procedure may be used

To 20 g of air dry pulp in a 500 ml Erlenmeyer flask add 250 ml of a solution containing 2 ml of glacial acetic acid and 10 g of sodium chlorite  $\text{NaClO}$  treat the pulp suspension to 80 C and hold at this temperature for approximately 30 minutes with occasional agitation Wash the pulp and make into several thin sheets Dry the sheets in an oven at 100 to 105 C for about 3 minutes and shred them Determine viscosity as specified under Procedure

2 When the viscosity pipet method is applied to pulps of very high viscosity it may be desirable to apply the solvent in two stages at two strengths to hasten solution of the samples A dilute solvent is used for wetting and swelling and a concentrated solvent is used for completion of dissolution The procedure used in this case is as follows

Weigh the equivalent of 0.125 g of moisture free pulp and introduce into the dissolving tube add 15 ml of a  $\text{Cu}(\text{En})_2$  solution adjusted to 0.167 copper molar and thoroughly wet the pulp sample with this solution Then add 10 ml of the cupriethylenediamine solution of 10 copper molarity Dissolve the sample in the usual manner This procedure gives 0.5% solution of cellulose in  $\text{Cu}(\text{En})$  (0.500 M in copper) and is equivalent to the standard procedure

3 Table 38.5 gives tentative correlation between various viscosity methods in use at the present time The 1%  $\text{Cu}(\text{En})_2$  viscosities at 25°C were determined according to the method given above The Picaunty seconds viscosities were determined according to the U. S. Army Specification No. 50.11.100B (May 27 1944) The 2.5% A. C. S. viscosities were determined according to the method described by the American Chemical Society<sup>59</sup> The viscosities determined by the TAPPI method were taken from a paper by Corey<sup>60</sup> The 1% cuprammonium viscosities were determined by the method given by Hatch Hammond and McNair<sup>61</sup> The 0.5%  $\text{Cu}(\text{En})$  capillary viscosities were obtained by preparing solutions of 0.5% concentration according to the method given above for the falling ball measurement but determining the actual viscosities with Cannon and Fenske capillary pipets

4 The procedures described above have been modified in some respects for application as routine mill control methods The necessary modifications are chiefly those involved in quick preparation of the test specimen Reference should be made to the original literature for details<sup>62 63 64 65</sup>

5 The falling ball method is to be applied to pulps at such concentration that the time of fall is more than 10 seconds and less than 40 seconds The viscosity pipet method can be applied to bleached pulps in any viscosity range provided the efflux time is within the limits specified in Table 38.5

<sup>59</sup> American Chemical Society Division of Cellulose Chemistry Ind Eng Chem Anal Ed 1, 49-51 1929

<sup>60</sup> Corey A. J. Tech Assoc Papers 27, 371 1944

<sup>61</sup> Hatch R. S. Hammond R. N. and McNair J. J. Tech Assoc Papers 25, 490 1942

<sup>62</sup> Hatch R. S. Pacific Pulp and Paper Ind 16, 13-17 Oct 1942

<sup>63</sup> Hatch R. S. Ind Eng Chem Anal Ed 16, 104-7 1943

<sup>64</sup> Levy R. M. Muffat P. and Harrison W. D. Paper Trade J 118, 20-31 Feb 1941

<sup>65</sup> Wood E. P. Tech Assoc Papers 27, 383 1944

TABLE 38-5. VISCOSITY CONVERSIONS<sup>66</sup>

1% Cu(En) <sub>2</sub> viscosity at 25°C. in cp.	Picatinny seconds	2.5% A.C.S. viscosity at 25°C. in cp.	Cuprammonium		0.5% Cu(En) <sub>2</sub> capillary viscosities at 25°C. in cp.	0.5% Cu(En) <sub>2</sub> capillary viscosities at 25°C. in cp.	TAPPI 1% cupram- monium viscosity at 20°C. in cp.
			1% Falling ball visc. at 20°C. in cp.	TAPPI 1% viscosity at 20°C. in cp.			
10	—	—	6	7.5	—	2	4
20	6.0	134	11	12	5.0	3	6
40	14.5	322	20	18.5	8.4	4	9
60	24.5	546	27.5	25	10.9	5	12
80	35	780	33	30	13.0	10	25
100	48	1070	39	36	14.8	15	38
120	61	1360	43	42	16.6	20	52
140	74	1650	48	46	18.1	25	70
160	88	1962	52	50	19.4	30	94
180	102	2275	56	54	20.6	35	124
200	117	2609	61	57	21.6	40	170
220	133	2966	65	61	22.6	45	224
240	150	3345	69	64	23.6	50	282
260	167	3724	72	67	24.5	55	340
280	184	4103	76	70	25.4		
300	202	4505	80	73	26.3		
320	220	4906	84	75	27.2		
340	239	5330	87	78	28.0		
360	258	5753	91	80	28.9		
380	277	6177	95	83	29.7		
400	297	6623	98	85	30.6		

## SOLUBILITY OF PULP IN SODIUM HYDROXIDE

AT 20°C.<sup>67, 68, 69, 70</sup>

This is a general cold-alkali solubility test for cellulose or pulp arranged for use with various and constant concentrations of caustic soda. The concentration of sodium hydroxide solution most frequently used is 18%. Concentrations of 5, 10, 21.5, and 50% are also employed depending on the use requirements of the pulp. For example, results with 21.5% have been shown to correlate in general with the yield of rayon in the viscose process.

This method avoids the sequential dilution step for the chosen concentration of sodium hydroxide as in TAPPI Standard T 203 m, p. 1751, and thus gives results that are not strictly comparable with it. This standard is considered to be more meaningful than T 203 m by the responsible committees in TAPPI, ASTM, and ACS. Also, here the soluble fraction of the pulp is determined rather than the insoluble residual fraction as in T 203 m. This avoids the acidification and washing of a residue with indeterminate effects.

The term "alpha-" cellulose should not be applied to any test value obtained with this procedure since it is defined only by the method of its determination

<sup>66</sup> Information in first six columns determined by Research Laboratory of the Weyerhaeuser Timber Co.; in last two columns by the Ecusta Paper Corp.

<sup>67</sup> Wilson, K., Ringstrom, E., and Hedlund, I., *Svensk Papperstidning*, 55, 31-37, 1952.

<sup>68</sup> Ohlsson, K. E., *Ibid.*, 347-57, 1952.

<sup>69</sup> Anon., *Ibid.*, 57, 193-94, 1954.

<sup>70</sup> Charles, Frank R., *Tappi*, 37, 148-56, April, 1954.

specified in T 203 m which in a modified form is being retained as a TAPPI Standard for alpha cellulose mainly for historical reasons

This procedure is recommended for general pulp evaluation and for purchase specifications

**Apparatus** **Stirring Equipment (Fig 38 19)**—The exact dimensions are not critical The stirrer and shell assembly is alkali resistant e g of stainless steel

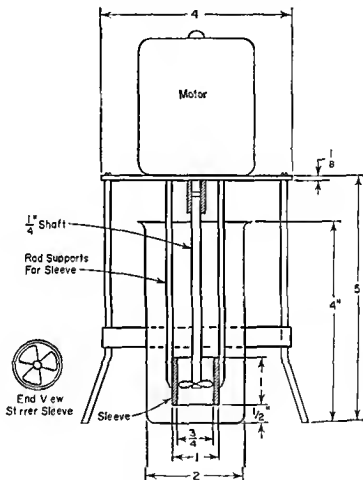


FIG 38 19 Stirring Equipment

A satisfactory motor is a  $\frac{1}{50}$  hp variable speed motor adjusted to go at about 1500 r p m The pitch of the blades or speed of the motor is adjusted so that no air is introduced into the pulp suspension during stirring

**Constant Temperature Bath**—Capable of maintaining a temperature of  $20 \pm 0.2^\circ\text{C}$  large size

**Filtering Crucible**—30 ml alkali resistant with fritted disc of coarse porosity (nominal maximum pore size 40 to 60  $\mu$ )

**Suction Flask** for the crucible

**Other Equipment** 10 and 100 ml pipets 250 ml beaker with watch glass cover 100 ml volumetric flask 250 and 1000 ml Erlenmeyer flasks with stopper for the 250 ml flask glass stirring rod

**Reagents.** **Sodium Hydroxide Solution.**—One of the concentrations below having an amount of sodium carbonate present less than 1 g. per liter.

To prepare the 18% solution, dissolve a quantity of solid sodium hydroxide in an equal weight of distilled water, cover and allow the suspended carbonate to settle, which may take several days, decant or siphon off the clear supernatant liquid, and dilute with carbon dioxide-free distilled water until the specific gravity at 20°/4°C. is  $1.1972 \pm 0.0012$  (the correction per degree Centigrade is 0.00051). Check the final dilution by a titration with standard acid. The  $\text{Na}_2\text{CO}_3$  content of the dilute solution should not exceed 1 g. per liter.

NaOH,  $5.0 \pm 0.1$  g. NaOH per 100 g. solution, sp. gr. is 1.0538 at 20°/4°C., 1.32 N.

NaOH,  $10.0 \pm 0.1$  g. NaOH per 100 g. solution, sp. gr. is 1.1089 at 20°/4°C., 2.77 N.

NaOH,  $18.0 \pm 0.1$  g. NaOH per 100 g. solution, sp. gr. is 1.1972 at 20°/4°C., 5.39 N.

NaOH,  $21.5 \pm 0.1$  g. NaOH per 100 g. solution, sp. gr. is 1.2356 at 20°/4°C., at 6.64 N.

NaOH,  $50.0 \pm 0.1$  g. NaOH per 100 g. solution, sp. gr. is 1.5253 at 20°/4°C., 19.07 N.

**Potassium Dichromate**, 0.4 N.—20 g.  $\text{K}_2\text{Cr}_2\text{O}_7$  with 150 ml. of concentrated  $\text{H}_2\text{SO}_4$  per liter.

**Sulfuric Acid.**—Concentrated (94–95%  $\text{H}_2\text{SO}_4$ , sp. gr. 1.84), reagent grade.

**Sodium Thiosulfate.**—About 0.1 N.  $\text{Na}_2\text{S}_2\text{O}_3$ , accurately standardized. (See TAPPI Standard T 610 m.)

**Potassium Iodide.**—Solid KI, reagent grade.

**Starch Solution**, 0.5%.—(Or Thyodene powder.)

**Test Sample.**—Obtain a sample of pulp that is representative of the entire lot being tested, weighing at least 5 g. for duplicate tests. If in sheet form, split, then tear into pieces approximately 5 to 10 mm. across. Do not cut with a pair of scissors nor use a grinder. If in slush form, dewater by suction, press between blotters to dry as much as possible and pull apart into small pieces. Spread the torn pieces on a tray open to the laboratory air for at least 24 hours, to attain uniform moisture content. At about the same time take composite specimens for the moisture and alkali solubility determinations.

**Procedure.**—With a pipet, add 100 ml. of the chosen NaOH solution to a 250-ml. beaker. Adjust the temperature, preferably by placing it in the constant temperature bath, to  $20 \pm 0.2^\circ\text{C}$ .

**NOTE.**—The solubility in 18% NaOH is not affected by variations of a few degrees in temperature. In this case the temperature may be kept at  $20 \pm 2^\circ\text{C}$ . The solubility in weaker alkali (for example 10% NaOH) is much more dependent on temperature. At this lower concentration, the temperature of the mixture should be maintained at  $20 \pm 0.2^\circ\text{C}$ ., even during subsequent disintegration.

Weigh, to the nearest 5 mg. or less, the equivalent of  $1.5 \pm 0.05$  g. of moisture-free pulp. At about the same time, weigh another portion and determine its exact moisture content in accordance with ASTM D644-55, p. 1804. Put the specimen into the alkali and allow it to swell for 2 minutes. Stir in the equipment for 3 minutes without aeration. This is sufficient time to defiber most pulps completely, which is essential. An increase in the stirring time does not significantly affect the solubility; too low a value will be obtained if defibering is not complete. Keep stirring, therefore, until the specimen is completely defibered. Lift the stirrer from the beaker. Carefully clean the stirring apparatus and walls of the beaker with a glass rod so that all pulp fibers will be retained in the caustic. Cover the

beaker with a watch glass and allow the beaker with the specimen to remain at  $20 \pm 0.2^\circ\text{C}$  for a period of 60 minutes from the time the specimen was added to the caustic

At the end of 60 minutes less the few minutes necessary to collect the filtrate stir the slurry with the glass rod and filter with suction through the fritted glass crucible. During filtration keep the cellulose mat on the filter covered with solution and be careful not to pull any air through it. Reject the first 10 to 20 ml and in a clean dry bottle or flask collect the next 40 to 50 ml of the filtrate for testing. If any suspended fibers are noticed in the filtrate pass the filtrate through the cellulose mat again to be clarified. Keep the filtrate in a stoppered Erlenmeyer flask and allow it to come to room temperature.

**NOTE**—During the early stages of the treatment the amount of material dissolved increases with the time of alkali leaching but after a certain time usually very little more is dissolved. For dissolving pulps 1 hour is usually sufficient but for some paper grade pulps such as hardwood neutral sulfite and some semichemical and sulfate pulps a longer time may be required. This should be checked by experiment. If a longer period than 1 hour is used the results will not be in accordance with this method and a special note should be appended to the results.

**Determination of Dissolved Cellulose**—Determine the cellulose in the filtrate by oxidation with the dichromate solution.

With a pipet transfer 10 ml of the filtrate to a 250 ml Erlenmeyer flask. Add 10 ml of 0.4 N  $\text{K}_2\text{Cr}_2\text{O}_7$  and then carefully add 30 ml of concentrated  $\text{H}_2\text{SO}_4$ . If the sulfuric acid is of lower concentration than 94% the temperature will not reach the required  $125^\circ$  to  $130^\circ\text{C}$  during the oxidation. Swirl to mix and apply heat to maintain a solution temperature of  $127 \pm 2^\circ\text{C}$  for a 10 minute period to complete the oxidation. Use of a reflux system for the flask is desirable.

Cool the flask to room temperature and quantitatively transfer the solution to a 1 liter Erlenmeyer flask using 500 ml of distilled water. Add approximately 2 g of solid KI swirl to dissolve and mix then allow to stand for 5 minutes. Titrate with the 0.1 N  $\text{Na}_2\text{S}_2\text{O}_3$  solution adding the starch indicator near the end point when the yellow color of the iodine has nearly disappeared. The end point occurs when the color of the solution changes from deep blue to light green. Make a blank determination substituting a 10 ml portion of the 18% (or other) NaOH solution for the filtrate and using approximately the same temperature and time to complete the titration.

**NOTE**—A 10 ml aliquot of the filtrate is sufficient for most dissolving pulps. For pulps having a very high solubility (greater than 16%) decrease the volume of the filtrate to 5 ml and the  $\text{H}_2\text{SO}_4$  to 25 ml. For highly insoluble pulps use a 20 ml portion of filtrate and 45 ml of  $\text{H}_2\text{SO}_4$ .

**Calculation**—Calculate the percentage of the pulp soluble in alkali as

$$\frac{(V_2 - V_1) \times N \times 6.85 \times 10}{W \times S}$$

where  $N$  = exact normality of the  $\text{Na}_2\text{S}_2\text{O}_3$ ,

$W$  = weight of the moisture-free pulp in grams,

$V_1$  =  $\text{Na}_2\text{S}_2\text{O}_3$  consumed in the titration of the specimen in milliliters,

$V_2$  =  $\text{Na}_2\text{S}_2\text{O}_3$  consumed by the blank in milliliters,

$S$  = milliliters of alkaline filtrate used in the oxidation, and

6.85 = milligrams of cellulose equivalent to 1 milliequivalent of  $\text{K}_2\text{Cr}_2\text{O}_7$ .



NOTE.—Theoretically 1 milliequivalent of  $K_2Cr_2O_7$  corresponds to 6.75 mg. of cellulose or polyoses, but under less ideal conditions of the oxidation described above, 1 milliequivalent corresponds to approximately 6.85 mg. of cellulose.

On each occasion the equivalence factor for the conditions and solutions employed may be determined as follows:

Without heating, dissolve  $0.2 \pm 0.001$  g. (moisture-free) of high-quality, bleached-cotton linters or ashless filter paper, in 40 ml. of 72%  $H_2SO_4$ , and in a 100-ml. volumetric flask, dilute to the mark with more 72% acid. Immediately thereafter, pipet duplicate 10-ml. aliquots of the cellulose solution into a pair of 500-ml. Erlenmeyer flasks, add 40 ml. 0.5  $N$  NaOH to each, and another 40-ml. portion of the NaOH to another flask as a blank. Oxidize and titrate the blank and each flask containing the 20 mg. of cellulose as described above. Suppose the results are  $V_3$  and  $V_4$  ml. respectively; then the equivalence factor (mg. of cellulose per ml. of  $N$  solution) or mg. of cellulose per 10 ml. of the 0.1  $N$   $Na_2S_2O_3$  as used—the portion replaced by the cellulose having been oxidized—is  $200/(V_3 - V_4)$ .

Take care that the 10-ml. pipet used to deliver the cellulose aliquot, is calibrated for the delivery of that solution, since it is more viscous than water. (Using the same 10-ml. pipet as was used for the specimen will minimize the possible error.)

Alternatively, in place of the KI and  $Na_2S_2O_3$  titration, after cooling the oxidized solution to room temperature, add 50 ml. of water to the specimen and to the blank. Cool again to room temperature, add 2 to 4 drops of ferrion indicator (1.5 g. *o*-phenanthroline monohydrate (or 1.6 g. of the hydrochloride) plus 0.7 g.  $FeSO_4$ , dissolved in water and diluted to 100 ml.) and titrate with a freshly standardized 0.1  $N$  solution of ferrous ammonium sulfate (40.5 g.  $FeSO_4(NH_4)_2SO_4 \cdot 6H_2O$  + 10 ml. concentrated  $H_2SO_4$  per liter) to a purple color. In the calculation above,  $V_1$  and  $V_2$  will represent the volume of ferrous ammonium sulfate used for the specimen and the blank, respectively. An electro-metric titrimeter is preferable for this titration.

Report.—Report to one decimal place the percentage of the moisture-free pulp which was dissolved by the alkali, and also the strength of the alkali solution used.

The strength of the NaOH solution may be designated by a numerical suffix, e.g., the solubility in 18% NaOH as  $x\%$  S18.

Precision.—The standard deviation for all NaOH concentrations is approximately 0.1.

*Additional Information.*—1. This solubility method may be applied to one particular pulp using several concentrations of alkali (5, 10, 18, 21.5%, etc.). The resulting relative solubilities may help to determine the suitability of the pulp for various industrial processes.

2. Reporting the difference between 100 and the percentage of alkali-soluble material in accordance with this, or any method other than "Alpha-, Beta-, and Gamma-Cellulose Pulp," as "alpha-cellulose" or "modified alpha-cellulose" or "new alpha-cellulose," is misleading and should be strongly discouraged.

# ANALYSIS OF PAPER

## SAMPLING PAPER FOR TESTING

**Test Sample**—The test sample, unless otherwise specified, shall consist (when possible) of specimens each cut not less than 11 by 11 in. This allows margin for trimming to exactly 10 by 10 in. which simplifies the calculation of basis weight determination. There shall be a sufficient number of specimens to complete the tests. They shall be kept smooth and flat and protected from exposure to direct sunlight, contact with liquids, and other harmful influences. Care should be exercised in handling the specimens if optical surface, acidity or other physical or chemical characteristics affected by the moisture of the hands are to be determined. In the case of a test for moisture the test sheets shall be placed, immediately after sampling in a can made airtight by means of a cover and kept in this condition until the moisture test is performed. Where an accurate moisture test is important it is desirable to take a separate sample for this and weigh the sample before opening the container. This method is standardized as ASTM D585-42 and TAPPI T 400 m 49.

**NOTE**—Physical tests except for weight shall not be made on portions of specimens in which there are flaws or watermarks.

**Procedure for Sampling**—The specimens comprising the test sample shall be so selected as to be representative of the entire lot of paper. One set of specimens shall be taken from 1 unit out of every 20 in the shipment, except that the minimum number of sets taken from a shipment shall be 5 and the maximum number 20. The same number of specimens shall be taken from each unit.

The units shall be rolls, cases, frames, skids or bundles.

In the case of rolls special care shall be taken to select test sheets that are not damaged. It is good practice, where moisture is not important to discard the first three layers of the roll, to be sure of obtaining a unit sample in good representative condition. When the moisture is to be determined, the sample shall not be taken within  $\frac{1}{2}$  in. of the outside of the roll. The specimens shall be cut from sheets taken across the full width of several unharmed layers.

In the case of sheet cut paper specimens shall be cut from at least five consecutive sheets taken from a point or points over  $\frac{1}{2}$  in. from the top or bottom of each case, frame, skid, or bundle sampled.

The specimens shall be trimmed with their edges exactly parallel to the machine and cross directions of the paper.

A sufficient number of specimens from each unit sample shall then be arranged consecutively in rotation to form a representative test sample. A convenient way to do this is to number consecutively the sheets comprising each set and then select sheets bearing consecutive numbers one or more from each set in rotation.

**Resampling**—In case of necessity for resampling a lot of paper, the samples shall be taken as described above, except that the sample sheets shall be taken from different units than those previously sampled.

## CONDITIONING PAPER AND PAPERBOARD FOR TESTING

This method is standardized as ASTM D685-44 and TAPPI T 402 m-49.

**Relative Humidity and Temperature.**—Whenever standard conditioning is required in a test method, the sample shall be conditioned and tested in an atmosphere maintained at 50% relative humidity and 23°C. (73°F.) temperature. A tolerance is permissible (unless for precise work) of plus or minus 2 in the percentage of relative humidity (48 to 52%) and of plus or minus 2°C. (3.5°F.) in temperature.

NOTE.—The wet-bulb temperature in degrees F., corresponding to a relative humidity of 50%, at a given air temperature,  $t^{\circ}\text{F.}$  (dry bulb), and a given barometric pressure,  $B$  inches of mercury, is given by the equation:

$$\text{Wet-bulb temp., } ^{\circ}\text{F. (50\% R. H.)} = 0.827t + 0.72 - 0.15(30 - B).$$

**Conditioning.**—Suspend each test specimen of the sample so that the conditioning atmosphere will have free access to all surfaces. Means shall be provided for so circulating the air of the conditioning and testing chamber that its humidity and temperature will be uniformly maintained. The conditioning time shall be sufficient for the moisture content of the specimen to attain equilibrium with the conditioning atmosphere. Determine this by conditioning until there is no significant change in the weight of the specimen (i.e., less than 1 part in 1000). For papers that are not highly resistant to water vapor, weigh at intervals of not less than 2 hours; for highly resistant papers such as hard, surface-sized bond and ledger papers, at intervals of not less than 12 hours; for papers that have been given special treatment for resistance to water vapor, and for paperboards, at intervals of not less than 24 hours.

NOTE.—With good circulation a conditioning period of 4 hours is usually sufficient for papers of ordinary weight and composition, but some hard-sized papers, paperboards, and water-resistant specialties may require 48 hours or longer.

After the test specimens are conditioned they should be handled as little as possible and not breathed upon.

For work of such precision that the hysteresis in the equilibrium moisture content may lead to an appreciable error, the moisture content equilibrium under standard conditions shall be approached from a drier state by first reducing, if necessary, the moisture content to less than half the value under standard conditions and then conditioning under standard conditions. For that purpose the samples may be dried in a desiccator or other convenient means, provided the temperature does not exceed 60°C. (140°F.).

**Determination of Humidity and Temperature.**—Determine the relative humidity of the conditioning atmosphere by means of either (1) a sling psychrometer, or (2) a stationary type of psychrometer having the air circulated over the thermometer bulbs mechanically. In both cases the circulation of air around the thermometer bulbs shall be at the rate of not less than 3 m. (10 ft.) per second and the exposure not less than 60 seconds before the readings are taken. When the sling type is used, make the readings, especially of the wet bulb, as quickly as possible after bringing it to rest.

NOTE.—It is preferable to draw the air over the thermometer bulbs rather than to blow it over them, as in the latter case the heat of the fan causes errors in the readings.

The thermometers used for determining humidity and temperature shall be accurately calibrated by comparison with certified standard thermometers and any corrections found necessary applied to the readings

NOTE—It is recommended that thermometers approaching the following specification be used Range 0 to 50°C (32 to 122°F) graduation 0.2°C (0.5°F) They should be

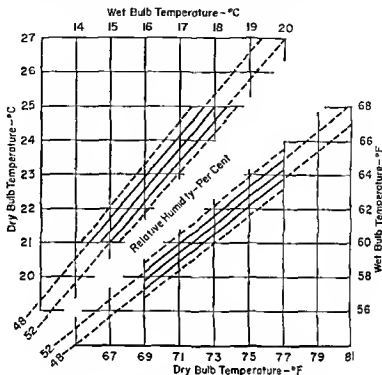


FIG. 38.20 Psychrometric Chart

matched to within 0.1°C (0.25°F) throughout the range used. Under ordinary conditions an error of 1 in the percentage of relative humidity corresponds to an error of approximately 0.25°I in the wet bulb depression.

From the wet bulb and dry bulb readings calculate the relative humidity from the accompanying psychrometric chart, Fig. 38.20.<sup>1</sup>

<sup>1</sup> Psychrometric chart for obtaining the relative humidity (in the neighborhood of the TAPPI Standard 50% R.H. and 23°C) from readings of a ventilated wet and dry bulb psychrometer. Permissible temperature and humidity conditions lie within the solid line parallelogram. The chart is based on a barometric pressure of 760 mm (30 in.) of mercury. For each 900 ft above sea level add 0.5. Example: Dry bulb temperature 21.2°C, wet bulb temperature, 17.5°C, elevation, 1700 ft above sea level. The corresponding relative humidity is 51 (from chart) + (1700/900 × 0.5) = 52%.

This chart is based on Smithsonian Meteorological Tables. For the information of those who wish to apply a correction with reference to a barometric reading, an elevation of 900 ft is approximately equivalent to 1 in. of mercury.

REDUCIBLE SULFUR IN PAPER AND PAPERBOARD <sup>72, 73, 74</sup>

This method is for determining the total reducible sulfur in paper, but is not necessarily a measure of how much a given paper will tarnish silverware. When tested by this method, paper that has less than 0.0008% reducible sulfur may be assumed to be nontarnishing as far as sulfur is concerned. A quantity greater than 0.0008% does not necessarily mean that tarnishing will occur, since sulfur compounds, which may not cause staining, are reduced by the treatment with the subsequent evolution of hydrogen sulfide. If more than 0.0008% reducible sulfur is found, or if the effect of that or other materials causing stains on silver is desired, the paper should be subjected to an accelerated tarnishing test.

**NOTE.**—If the pH of the paper is low, e.g., 4 to 4.5 (cold extraction), as little as 0.0002% of reducible sulfur may cause tarnishing of imitation gold-bronze prints; whereas, if the pH were higher, e.g., on brush-coated art paper, a much higher quantity of sulfur might be tolerated.

Because this is a very sensitive test method, and the quantities of sulfur sought are so small, great care must be taken to avoid possible contamination of the reagents and specimens by contact with the bare fingers, or from minute quantities of sulfur compounds being absorbed from the air. Consequently, even if a day elapses between tests, it is advisable to make a blank test with the same apparatus, liquids, and materials to be used for the actual test, to make sure that they neither contain, nor have acquired, any appreciable quantity of sulfur.

**Apparatus.** *Reaction Apparatus.*—An apparatus consisting of a 100-ml. extraction flask carrying a short, water-cooled condenser as shown in Fig. 38-21. Over the condenser is placed a flanged head containing a disc of filter paper impregnated with lead acetate. The condenser prevents water vapor from condensing on the test paper which would cause an uneven development of the spots.

*Buret or Pipet.*—1 ml., graduated in 0.01-ml. divisions.

*Other Equipment.*—Water bath at 100°C. or steam bath, to heat the reaction flask; 50-ml. beaker and glass stirring rod with flattened end; 100-ml. and 1-liter volumetric flasks; 10-ml. pipet, and clean forceps for handling the specimens.

*Reagents.* *Aluminum Foil.*—Not over 0.01 in. thick, sulfur free.

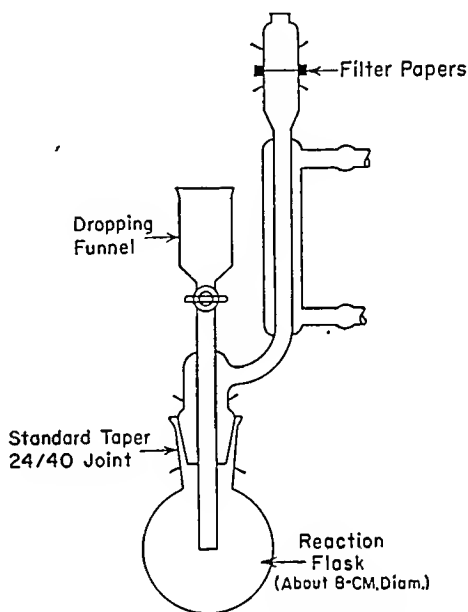


FIG. 38-21. Apparatus for Reducible Sulfur.

<sup>72</sup> Schere, P. C., and Sweet, W. W., *Ing. Eng. Chem., Anal. Ed.*, 4, 103, 1932.

<sup>73</sup> Lachele, C. E., *Ind. Eng. Chem., Anal. Ed.*, 6, 200, 1934.

<sup>74</sup> Sutermeister, Edwin, *Chemistry of Pulp and Paper Making*, 3rd ed., John Wiley and Sons, New York, p. 472, 1941.

**Phosphoric Acid**—Concentrated 85%  $\text{H}_3\text{PO}_4$  reagent grade sulfur free. It is advisable to treat the acid with bromine water and heat until all excess bromine is expelled.

**Sodium Thiosulfate**—Standard solution not over two days old. Use recently boiled distilled water cooled to about  $20^\circ\text{C}$  for preparing the solution. Dissolve 0.091 g of reagent grade fresh clean crystals of  $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$  in a little water in a 100 ml volumetric flask dilute to the mark and mix thoroughly. Then dilute 10 ml of this solution to 1 liter and mix thoroughly. One ml of this diluted solution contains the equivalent of 0.0000025 g of sulfur.

**Lead Acetate**—20% solution  $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot 3\text{H}_2\text{O}$  reagent grade.

**Test Paper**—Fresh high quality rapid filtering grade of filter paper untouched with bare fingers and impregnated with the lead acetate solution dried and cut into 1 in diam discs and to be kept stored in an air tight container. Cut also 1 in diameter discs of the unimpregnated paper to clamp beneath each test disc so as to prevent any acid spray decolorizing the darkened areas. Just before use pick up a disc of the test paper with clean forceps moisten with a minimum of distilled water and lay it on a dry unimpregnated disc ready to go into the apparatus.

**Test Specimen**—For each test specimen cut pieces of paper about 6 mm ( $0.25$  in) square from representative sample sheets and weigh the equivalent of  $0.25 \pm 0.005$  g of moisture free paper. (Determine the average moisture content of the paper if it is not known to within 1%.) For papers which are low in sulfur increase the weight of the test specimen preferably to 0.5, 0.75 or to a maximum of 1 g. Do not touch the test area of the specimen with the fingers. Handle with clean forceps only.

**NOTE**—Tightly wrap any samples that are to be stored or shipped in such a way as to be in sulfur free aluminum foil.

**Procedure**—By means of the forceps transfer the weighed specimen to the flask. Add a few milliliters of distilled water and macerate the paper by means of a clean glass stirring rod until it is thoroughly soaked and at least partially disintegrated. Wash down the glass rod with a few milliliters of distilled water until the total volume in the flask is about 20 ml. Add 2 g of aluminum foil cut in small pieces. Attach the condenser, the funnel and the head containing the disc of lead acetate paper with the plain paper disc beneath to the flask. Through the dropping funnel add 10 ml of  $\text{H}_3\text{PO}_4$  and close the cock. Heat the flask and contents on the water bath. After 45 minutes remove the apparatus from the bath, take out the lead acetate disc, compare it with the set of discs stained with known amounts of sulfur prepared as described below and estimate the amount of sulfur evolved by the specimen.

Prepare the set of stained discs by using exactly the same procedure and chemicals as described but in place of the test specimen from the graduated pipet or buret add measured amounts of the standard  $\text{Na}_2\text{S}_2\text{O}_3$  solution such as 0.1, 0.2, 0.4, 0.6, 0.8 and 1.0 ml respectively. This will give a range suitable for most papers. One milliliter of this solution contains the equivalent of 0.001% sulfur in a 0.25 g specimen.

Before each series of tests make a blank test using the same amounts of water, acid and aluminum foil as used in the procedure but without any additive. The resulting stain should be barely perceptible otherwise purify or replace the reagents or clean the equipment.

**Report.**—Report the amount of reducible sulfur as a percentage by weight of the moisture-free paper, to two significant figures.

**Additional Information.**—A modified colorimetric method, comprising the reduction of the sulfur to hydrogen sulfide and reaction with *p*-aminodimethyl aniline to form methylene blue, has been described.<sup>74a</sup> This method will be considered in a subsequent revision of the method when additional correlative data are obtained.

It is probable that if the prescribed reduction method with aluminum foil, is used in place of the more drastic sodium stannite reduction method described in Sobolev, the results will be the same with either the lead acetate or the methylene blue indicator.

### AMOUNT OF COATING ON MINERAL-COATED PAPER

This method is suitable for the ordinary types of mineral coatings. It may not be effective for exceptional special types, as where lacquers or other materials are used to impart a high degree of water resistance. This method is standardized as ASTM D687-44 and TAPPI T 407 m-49.

**Reagent. Enzyme Solution.**—Aqueous solution of approximately 1.5 g. of enzyme and 25 ml. of 0.1 N NaOH per liter.

The enzyme recommended by Sutermeister and Porter<sup>75</sup> is trypsin, but some of the mixtures of enzymes used commercially for desizing cotton and degumming silk have been found to be more rapid in action, less expensive, and more stable.<sup>76</sup>

**Test Specimen.**—The specimen for test shall consist of not less than 25 sq. in. Before weighing it shall be conditioned according to TAPPI Standard T 402 m. After removing the coating, the residual paper shall be likewise conditioned before weighing.

**Procedure.**—Measure the area of the test specimen with an accuracy of  $\pm 0.5\%$ . (If the test specimen is 5 by 5 in., this requires measuring the length and width to the nearest 0.025 in. or about 1/32 in.) Weigh the test specimen with an accuracy of  $\pm 0.5\%$ . (For lightly coated papers this requires weighing to the nearest 0.005 g.; for heavily coated papers, it may require only the nearest 0.05 g.)

Place it in a suitable container in such a way that the enzyme solution will have free access to the entire surface of the coating. It may be laid in a flat-bottomed tray or rolled in cylindrical form and placed in a buret. Pour over the specimen sufficient enzyme solution to cover it completely. Allow to stand for at least 1 hour at 50°C., then place the paper on a pane of glass and brush off the coating with a camel's hair brush, taking care not to dislodge the paper fibers. Additional heating, and in some cases additional enzyme solution, may be found necessary for very resistant coatings.

After the coating is entirely removed, stand the glass pane at a slight angle and wash the paper on both sides by means of a wash bottle, holding the paper on the glass by one corner. Condition the decoated paper and weigh it. The difference between this weight and the original weight of the specimen is the amount of

<sup>74a</sup> Sobolev, I., Bhaigava, R., Gosuntov, N., and Russell, R., TAPPI, 39, No. 9, 628-30, 1956.

<sup>75</sup> Sutermeister, E., and Potter, Tech. Assoc. Papers 13, 205, 1930.

<sup>76</sup> The preparation Protease 15, made by Röhm & Haas Co., 222 West Washington Square, Philadelphia, Pa., has been found suitable.

coating material. Not less than two determinations shall be made and the average of the results shall be reported.

**Report**—The amount of mineral coating shall be reported (1) as a percentage of the decoated paper and (2) as pounds per 500 sheets 25 x 40 in in size. The weight of the decoated paper on this same weight basis shall also be included in the report.

**Precision**—Owing to the variable nature of coating materials the precision is variable. With most ordinary types of coatings the percentage of coating material found should be correct to within 0.5 to 2.

## ROSIN IN PAPER AND PAPERBOARD

Rosin (colophony) is a natural resin extracted from the residue of the distillation of pine gum, tall oil, or the solvent extract of pine stumps, knots, and tops.

This method is for both the qualitative and quantitative determination of rosin in paper and paperboard. The qualitative tests indicate the presence or absence of rosin or rosin soap added as a sizing agent. The quantitative procedures give the total rosin, which consists of the natural resins in the pulp from which the paper was made plus any rosin added as sizing. The procedures described are not applicable to the determination of synthetic resins (such as the melamine and urea formaldehyde resins used to impart wet strength properties to paper) but are limited to rosin. This method is standardized as ASTM D549-46 and TAPPI T 408-06.

## QUALITATIVE TESTS

**Apparatus** Crucible, porcelain 35-50 ml

**Spotting Plate**—Porcelain or white glass with depressions

**Reagents** Acetic Anhydride

Sugar—Saturated solution of sucrose

Sulfuric Acid—Concentrated  $H_2SO_4$

Carbon Tetrachloride  $CCl_4$

Bromine Liquid Br

Phenol

**Procedures** **Liebermann-Storch Test**—Place about 1 g of the paper cut into small pieces in a clean dry test tube. Add 5 ml of acetic anhydride and boil down to about 1 ml. (*Caution*—Since fumes of the anhydride are very irritating the test should be made in the hood.) Pour the liquid residue into a clean dry porcelain crucible and cool to room temperature or lower. If any waxy particles separate out they should be filtered off on a small piece of filter paper previously wetted with acetic anhydride. Add carefully down the side of the crucible one drop of concentrated sulfuric acid. A fugitive rose-violet coloration formed where the acid meets the anhydride indicates rosin.

**Raspail Test**—Place the paper on a glass or porcelain plate and apply a drop of nearly saturated solution of sugar. After about 5 seconds remove the excess sugar solution by blotting with filter paper. Add a drop of concentrated  $H_2SO_4$  to the sugar on the paper. Alternatively place a drop of concentrated  $H_2SO_4$  on the paper and add a few crystals of sugar to the drop of acid. A raspberry-red coloration indicates the presence of rosin.

**Halphen-Hicks Test**—This test consists of bringing a carbon tetrachloride extract of the specimen into contact with bromine vapor and seeing if a violet color



ation forms. The reaction with common rosin is so intense that if present in any considerable amount, the violet color is apt to be masked. The test also can be applied to solid resins, varnishes, etc. The presence of more than a trace of water, alcohol or ether, interferes with the sensitiveness of the reaction.

Prepare two solutions: Solution *A*, 1 part of phenol dissolved in 2 parts by volume of  $\text{CCl}_4$ ; and Solution *B*, 1 part of Br dissolved in 4 parts by volume of  $\text{CCl}_4$ .

Place about 1 g. of the paper, cut into small pieces, in a clean, dry test tube. Add about 3 ml. of solution *A*, and shake or macerate with a stirring rod for several minutes. Pour the solution into one of the cavities of the spot plate until it just fills a depression; a portion of the solution will soon be seen to spread out on the flat part of the plate beyond the rim of the cavity unless too much of the  $\text{CCl}_4$  previously has been lost through evaporation. If it does not spread, a drop or two more of  $\text{CCl}_4$  should be added to produce this spreading effect.

In an adjacent cavity of the plate, immediately place 1 ml. of solution *B* and be sure the evolved Br vapors come into contact with the surface of the solution in the other cavity, either by blowing a gentle current of air toward it or by covering both cavities with a watch glass.

The color reaction begins almost immediately, and the colors are best observed upon the flat portion of the test plate. They usually last long enough for satisfactory observation, with their changes being practically complete in from 5 to 10 minutes.

If a green color develops which rapidly changes to blue and then violet, the latter lasting a considerable time, then slowly to purple, and finally to a deep indigo, rosin is indicated.

The intensities of the colors and tints are, of course, dependent to a degree upon the concentration of the rosin dissolved in solution *A*, but with a little experience in the application of the test to materials of known purity, it is possible to interpret the indications without difficulty.

Different colors may be produced by different materials with these tests as follows:

## CHARACTERISTIC COLORS

<i>Material</i>	<i>Liebermann-Storch</i>	<i>Halphen-Hicks</i>
Rosin	Fugitive violet to brown	Blue, finally indigo
Oxidized rosin	Fugitive violet to brown	Blue
Rosin glycerol ester	Fugitive violet to brown	Lavender-blue
Staybelite <sup>a</sup>	Fugitive violet to brown	Lavender-blue
Rosin maleate	Wine red changing to olive brown	
Beta-pinene polymer	Faint pink	Faint brown
Vinsol <sup>b</sup>	Weak purple	Green-brown
Belro <sup>c</sup>	Weak purple-brown	Green-brown
Pine oil	Red-brown to blue-violet	
Turpentine	Faint yellow to red	...

<sup>a</sup> Pale-colored hydrogenated rosin.

<sup>b</sup> Aliphatic hydrocarbon-insoluble fraction of a solvent extract of aged pine stump wood.

<sup>c</sup> Dark rosin fraction from the solvent refining of wood rosin.

## QUANTITATIVE DETERMINATION

The method depends upon the conversion of insoluble resins to alcohol soluble rosin followed by extraction. The conversion is effected by the action of hydrochloric acid of a definite concentration for a given time so as to limit the formation of other hydrolysis products. The dried extract is further extracted with anhydrous ether in which nonresinous materials including starches and glues, are insoluble. If unsaponifiable waxes which may dissolve in anhydrous ether are also present they are separated from the resinous material by saponification of the rosin. Further details are given below.<sup>77</sup>

Qualitative tests may also be applied for the presence or absence of mineral matter which reacts with or is dissolved by HCl for example a carbonate filler and for the presence of paraffin or a similar wax to serve as guides for the subsequent analysis.

It has been found<sup>78</sup> that melamine formaldehyde resin does not interfere with the determination of rosin.

**Apparatus** Extraction Apparatus Soxhlet or Underwriters

Gooch Crucible—30–50 ml with fine pore filter papers cut to fit

Suction Flask for Gooch Crucible

Beaker 30–50 ml

If waxes are also present

Separatory Funnels Two 250 ml or larger

Reflux Flask and Condenser—250 ml flask or larger

Steam Bath for Reflux Flask

**Reagents and Materials** Hydrochloric Acid Concentrated and approx 1 N HCl

**Extraction Solvent**—Mixture of 4 ml of concentrated HCl in 1 liter of 95% ethyl alcohol

**Ether**—Diethyl anhydrous peroxide free

If waxes are also present

Potassium Hydroxide 5% alcoholic solution KOH

Sodium Chloride—NaCl crystals

Sulfuric Acid—Approximately 5 N H<sub>2</sub>SO<sub>4</sub>

Methyl Orange Indicator 0.1% aqueous solution

**Test Specimen**—For each test prepare at least 10 g of specimen about 0.25 by 1.6 in (6 × 40 mm), cut from representative samples taken in accordance with TAPPI Standard T 400 m p 1794. The paper should not be ground since additional nonresinous materials may then be extracted.<sup>79</sup>

**Procedure**—Allow the specimen strips to reach moisture equilibrium with the atmosphere surrounding the balance and weigh 5 to 7 g of strips to the nearest 0.01 g. Unless known to within 1% determine the moisture content of a separate specimen similarly conditioned according to ASTM D644-55 p 1804.

If the paper contains mineral matter reacting with or dissolved by hydrochloric

<sup>77</sup> Launer H F Simplified Determination of Resin in Papers and Pulps Resea ch Paper RP973 J Res Nat Bureau Standards 18, No 2 Feb 1937

<sup>78</sup> Wilson W K Harvey J L and Padgett W A TAPPI 34 No 9 419 1931

<sup>79</sup> For paperboard such as container board pressboard binders board and pasted board it is advisable whenever possible to split the strips into thinner ones after they have been weighed to facilitate extraction of the resin.

acid, immerse the test specimen to be extracted in *N* HCl for 5 minutes, drain, wash free from acid, and dry at room temperature.

Crease the strips to be extracted with small zigzag folds and place them lengthwise in the siphon cup of the extractor, taking care to avoid packing them tightly together. To the extractor, add from 2 to 2.5 times the volume of the extraction solvent required to fill the siphon cup. Extract at the rate of 15 siphonings per hour (which should yield a volume of about 250 ml. of solvent distilled per hour). A period of 2 hours should be used for uncoated or nonsurface-sized papers and 2.5 hours for coated or surface-sized papers, or for paperboards. The extraction should not be continued much longer than specified, since resinous materials other than rosin might possibly be extracted and reported as rosin.

When the extraction period is completed, evaporate off the solvent in the flask on the steam bath, until the odor of alcohol and HCl are no longer noticeable. Place the flask in an oven at  $105^{\circ} \pm 3^{\circ}\text{C.}$  for 15 minutes, cool to room temperature, and add 20 ml. of anhydrous ether. The rosin should dissolve in from 5 to 30 seconds unless covered by foreign material, in which case it should be scraped with a stirring rod. Unless the ether solution is clear, allow to stand 15 to 20 minutes to further the coagulation and settling out of the foreign matter. Filter the solution, including the rinsings from the flask with about 20 ml. of ether, through the Gooch crucible with the fine-pore filter paper, and transfer the solution to a carefully dried and weighed beaker. It is often necessary to refilter the solution through the same paper to remove cloudiness. After filtering, rinse the filter with less than 20 ml. of ether. Evaporate the ether in the tared beaker; then dry in an oven at  $105^{\circ} \pm 3^{\circ}\text{C.}$  for 15 minutes, cool, and weigh to the nearest 1 mg. Repeat the drying and weighing until the weight is constant to  $\pm 1$  mg. (*Caution.*—Do not place ether-wet material in an oven with exposed electrical contacts.)

If paraffin or similar waxes are present, after weighing the beaker plus rosin and wax, add about 25 ml. of approximately 0.5 *N* alcoholic KOH solution, heat to not over  $60^{\circ}\text{C.}$  for 15 minutes, cool to room temperature, and transfer to a separatory funnel. Wash the beaker with about 25 ml. of ether and then with about 50 ml. of water, and add all washings to the separatory funnel. Add sufficient water or ether, or both, so that the funnel contains about 25 ml. of ether and 150 ml. of water. Shake the funnel well, add about 2 g. of NaCl, shake the funnel once more, and allow separation of the liquids. Draw off the water solution into another separatory funnel and wash with 25 ml. of ether. Drain the two ether solutions into a beaker, wash both funnels with about 20 ml. of ether, adding the washings to the beaker, and evaporate the ether. Treat the dry residue with anhydrous ether and filter the resulting suspension through glass wool or fine porosity fritted glass to remove any NaCl and evaporate the filtrate in a weighed beaker. Dry the beaker and residue at  $105^{\circ} \pm 3^{\circ}\text{C.}^{80}$  for 15 minutes, cool, and weigh to the nearest 1 mg. Repeat the drying and weighing until the weight is constant to  $\pm 1$  mg. The material thus obtained will be paraffin or similar wax, plus the unsaponifiable material from the rosin, which, for most purposes and in the absence of definite knowledge regarding the particular rosin in the paper under test, may be assumed to be 5% of the rosin in the paper. To obtain the weight of the rosin therefore, divide the weight of the combined rosin and wax, less the weight of the wax, by 0.95.

<sup>80</sup> If the paper contains waxes or oil volatile at  $105^{\circ} \pm 3^{\circ}\text{C.}$  and it is not practicable to dry the residue at a lower temperature, separate the rosin from the oil by saponification and determine it directly, as prescribed in the following alternative method.

**Alternative Treatment of Rosin Wax Extract Where a Direct Determination of the Rosin is Desired**—Wash the weighed rosin wax residue obtained from the alcohol extracted paper into a wide mouthed flask using about 25 ml of ether. Add about 25 ml of approximately 0.5 N alcoholic KOH and about 100 ml of water. Heat the contents of the flask to boiling under a reflux condenser for 30 minutes, cool to room temperature, add about 25 ml of ether, transfer to a separatory funnel and wash the flask first with water and then with ether, adding the washings to the funnel. Add about 2 g of NaCl to the separatory funnel, shake well and let the liquids separate. Draw off the water solution into a beaker. Add 50 ml of water and about 2 g of NaCl to the ether solution in the separatory funnel, shake well, allow separation of the two liquids and draw off the water solution, adding it to the first water solution.

Add to the combined water solutions 2 drops of methyl orange indicator solution, carefully acidify by adding 5 N  $\text{H}_2\text{SO}_4$  until the solution is definitely pink and then add 1 ml more of the acid. Cool the solution to room temperature, transfer to a separatory funnel, add 25 ml of ether and wash the beaker with about 10 ml of ether, adding the washings to the funnel. Add about 5 g of NaCl, shake the funnel well, allow separation of the liquids, draw off the water solution into another separatory funnel and wash it twice more, using about 20 ml of ether each time. Transfer all ether solutions to a weighed beaker, washing all containers with ether. Evaporate the ether dry in an oven at  $105^\circ \pm 3^\circ \text{C}$  for 1 hr and weigh to the nearest 1 mg. Repeat the drying and weighing until weight is constant to  $\pm 1 \text{ mg}$ . The weight of the rosin thus found is assumed to be 95% of that in the paper.<sup>81</sup>

**Report**—Report the results as the average of at least two determinations to the nearest 0.1 as a percentage by weight of the moisture free paper.

**Precision**—Ninety five per cent of the time the results of duplicate determinations may be expected to agree within 0.2%.

## MOISTURE IN PAPER, PAPERBOARD, AND PAPERBOARD AND FIBERBOARD CONTAINERS

This method covers the procedure for determining moisture in all papers, paperboards and paperboard and fiberboard containers except those containing material other than water that is volatile at  $105^\circ \text{C}$ . This method is standardized as ASTM D644-55.

**Apparatus** **Weighing Container**—Airtight for weighing the specimen before and after drying. A glass weighing bottle with a ground stopper is suitable for specimens of the order of 2 g. The weighing bottle may be of either high or low form, a volume of about 100 ml is appropriate. An airtight metal container preferably containing a lightweight large mesh wire basket is suitable for larger specimens, particularly those over 10 g.

**Thermometer**—To indicate the temperature of the drying oven. This thermometer shall include the temperature range of 100 to  $110^\circ \text{C}$  and its scale shall be divided in 1 degree intervals.

<sup>81</sup> If the paper contains saponifiable fats or greases in addition to rosin, the alternate method described above will give results higher than the true rosin content as they will be included with it. In this case the analyst may apply such modifications to the method as are considered justifiable and the report should state what modifications of the standard method were used.

**Drying Oven.**—Constant-temperature, equipped with means for insuring adequate temperature control and air circulation, and preferably equipped with means for drying the air entering the oven.

**Chemical Balance.**—Sensitive to 1 mg., for weighing specimens of 2 g. and under, and sensitive to 0.05% of the original weight of the specimen for larger specimens.

**Desiccator.**—In which weighing containers and specimens are cooled after drying. It is recommended that anhydrous alumina (indicator grade) be used as the desiccant.

**Test Specimens.**—When moisture is determined for the purpose of calculating the results of a chemical analysis of paper or board on a moisture-free basis, the test specimens shall weigh not less than 1 g., and preferably not less than 2 g. each. At the time of initial weighing, these specimens shall be in moisture equilibrium with the samples being analyzed.

When moisture is determined for the purpose of calculating the amount of moisture in a shipment, the test specimens shall weigh not less than 50 g. each, and shall be taken from samples obtained in accordance with the Standard Method of Sampling Paper and Paper Products (ASTM Designation: D585).

When moisture is determined on combined board or containers that are to be tested for other physical properties, test specimens shall weigh approximately 50 g., and shall be taken so as to be representative of the material being tested. In the case of containers, specimens shall be cut from unsealed sections, and preferably from unprinted sections, of the container, and shall be taken from each type of container being tested.

**Procedure.**—Determine the tare weight of the oven-dried weighing container as follows: Heat the open container (container, stopper or cover, and wire basket, if any) in the oven at  $105 \pm 3^{\circ}\text{C}$ . for 1 hour. At the end of that period, quickly close the container, remove it from the oven, and place it in the desiccator to cool for 1 hour. Remove the closed container from the desiccator, momentarily loosen the cover to equalize the pressure, and then weigh the container.

Transfer the test specimen to the tared weighing container as soon as the specimen is withdrawn from the sample of material under test and close the container immediately. Great care must be taken to avoid change in moisture content during the transfer of the specimen from the sample to the container. Handle the specimen with tweezers or clean, dry rubber gloves. If a delay of over a second or two in transferring the specimen to the container is unavoidable, keep the specimen covered on both sides with several adjacent layers of the paper or board from which it is withdrawn, until it can be placed in the container. Then discard the protecting layers of paper or board. Unless the specimen is later to be spread out in the oven, avoid filling the container tightly. Weigh the closed container holding the test specimen, to allow calculation of the original weight of the specimen. The weighing container should not be touched with the fingers during these manipulations.

Remove large specimens from the container. If the container has a removable basket, leave the specimen in the basket, and place the basket and open container in the oven. If the container does not have a removable basket, spread the specimen in a basket or tray which will permit free circulation of air around the specimen, and place the basket or tray and the open container in the oven. Heat for 2 hours at  $105 \pm 3^{\circ}\text{C}$ . Replace the specimen in its container and close the container, doing this, if possible, without removing the specimen from the oven. Place

the closed container in the desiccator and allow it to cool for 1 hour. Loosen the top of the container momentarily to equalize the pressure and then weigh the container to allow calculation of the oven dry weight of the specimen.

Place small specimens in the drying oven without removing them from the weighing bottle. Remove the stopper of the bottle. Heat for 1 hour at  $105 \pm 3^\circ\text{C}$ . Close the bottle in the oven. Cool to room temperature in the desiccator and weigh. Remove the stopper momentarily just before weighing to equalize the pressure.

Repeat the required drying and weighing operations until the difference in weight between two successive weighings is not more than 0.1% of the weight of the specimen.

Make all weighings to the nearest 1 mg for specimens of the order of 2 g and weigh to within 0.05% of the weight of the original specimen for specimens over 2 g.

**Calculation**—When the percentage of the moisture based on the original weight is required, it shall be calculated as follows:

$$\text{Moisture per cent} = \frac{W_1 - W_2}{W_1} \times 100$$

where  $W_1$  = original weight of the specimen and

$W_2$  = weight of the specimen after oven drying.

When the percentage of moisture based on the oven dry weight is required, it shall be calculated as follows:

$$\text{Moisture per cent} = \frac{W_1 - W_2}{W_2} \times 100$$

where  $W_1$  = original weight of the specimen and

$W_2$  = weight of the specimen after oven drying.

**Report**—Report the moisture as the percentage loss in weight of the specimen to the nearest 0.1% on the basis of the original weight or on the oven dry basis.

**Reproducibility of Results**—The results of duplicate determinations of moisture should agree within 0.2%.

## ASH IN PAPER

The ash content of paper is defined as the residue after complete combustion at  $925 \pm 25^\circ\text{C}$  ( $1697 \pm 45^\circ\text{F}$ ). The ash may consist of (a) various residues from chemicals used in paper manufacture, (b) metallic matter from piping and machinery, (c) filling, coating and pigmenting materials, and (d) mineral matter in the pulp from which the paper was made. In general, if the ash content does not exceed 1 to 2%, no filling, coating or pigmenting material has been added, although pigments, especially titanium pigments, are sometimes used in very small amounts. When filling and coating materials are present, which do not change much on ignition, the ash is an approximate measure of the amount added. This method is standardized as ASTM D586-42 and TAPPI T 413 m 58.

**Apparatus** **Crucible**—A platinum crucible or dish with lid or cover is recommended. If not platinum, porcelain or silica crucibles may be used, provided they have previously been well baked at  $925^\circ\text{C}$  or more, so that their weight does not change upon ignition.

**Analytical Balance.**—Having a sensitivity of 0.1 mg. and with class S weights.

**Electric Muffle Furnace.**—Adjusted to maintain a temperature of  $925 \pm 25^{\circ}\text{C}$ .

**Test Specimen.**—Obtain a representative sample of the paper and weight out a test specimen, preferably in duplicate, consisting of small pieces of the paper weighing enough to yield at least 10 mg., and preferably more, of ash.

Determine the moisture content of the paper if not known by drying a representative portion to constant weight at  $105 \pm 3^{\circ}\text{C}$ . This may be done, if convenient, in the ignited and weighed crucible used for ashing the paper.

**Procedure.**—Carefully clean the empty crucible and ignite in a muffle furnace at  $925 \pm 25^{\circ}\text{C}$ . After ignition, cool slightly and then place in a desiccator, preferably containing indicating-grade, anhydrous alumina. When cooled to room temperature, weigh the ignited crucible on the analytical balance to the nearest 0.1 mg.

If of a suitable size, place the specimen in the crucible and burn the paper directly over a low flame of a Bunsen burner, or preferably on the hearth of the furnace, until it is well carbonized. If the crucible is too small to hold the entire specimen, gently burn the portion added and add more as the flame subsides. Take care not to blow portions of ash from the crucible. Continue heating with the burner only as long as the residue burns with a flame. When the flame has died down, place the crucible in the furnace at  $925 \pm 25^{\circ}\text{C}$ . for a period of at least 3 hours, or longer if needed to burn away all the carbon. If a lid or cover is used, as is desirable, place it on the crucible during the initial ignition of the paper at  $925^{\circ}\text{C}$ . and when the crucible and contents are red hot, slide it off to allow the combustion to be completed.

When the paper is completely burned as indicated by the absence of black particles, remove the crucible from the furnace, replace the cover, and allow to cool somewhat. Then place in a desiccator and cool to room temperature. Reweigh with the ash to the nearest 0.1 mg. and repeat the weighing and ignition until the weight is constant. Calculate the percentage of ash based on the moisture-free weight of the paper.

**Report.**—Report the ash as a percentage of the moisture-free paper to the nearest 0.05 for papers containing 5% ash or less, to the nearest 0.1 for papers containing 5 to 10% of ash, and to the nearest 0.2 for papers containing over 10% of ash.

**Precision.**—The results of duplicate ash determination should be suspect if they differ by more than amounts indicated in Table 38-6.

TABLE 38-6. PERMISSIBLE DEVIATIONS BETWEEN DUPLICATES

<i>Weight of Ash, mg.</i>	<i>Maximum Permissible Difference, mg.</i>
Over 50	3
20-50	2
10-20	1

**Additional Information.**—1. Because the ignition temperature usually affects the weight of the ash considerably, only values obtained at  $925 \pm 25^{\circ}\text{C}$ . should be reported as being in accordance with this Standard.

2. Paper normally contains added mineral matter which becomes the main constituent of its ash, and which is modified at high temperatures to different degrees depending on its composition. Accordingly it has appeared desirable to select the

higher temperature of 925°C as compared with the 575°C for wood or pulp in order to gain better reproducibility

3 The main change in this revision is to add the limits of  $\pm 25^\circ\text{C}$  to the specified ignition temperature

### CASEIN IN PAPER (QUALITATIVE)

This method is applicable only to papers in which the amount of casein is relatively large for example mineral coated papers in which casein is commonly used as the binder It is not applicable to papers containing such small amounts of casein as may be used in the beater furnish as a constituent of the engine sizing etc This method is standardized as ASTM D587-42 and TAPPI T 415 m-43

**Reagent** Millon's Reagent Dissolve 20 g of pure mercury in 40 g of pure concentrated nitric acid ( $\text{HNO}_3$ ) and dilute the solution to 180 ml with distilled water

**Test Specimen**—The specimen shall consist of about 0.5 g of paper cut in small pieces It shall be so selected as to be representative of the sample

**Procedure**—Boil the specimen several minutes in a test tube with 10 ml of 1% caustic soda solution (Caustic soda is required to dissolve casein that has been hardened by formaldehyde or other agent) Filter off the aqueous extract cool to room temperature add a suitable indicator such as phenolphthalein and exactly neutralize with nitric acid Add several ml of the Millon's reagent On heating the presence of casein is indicated by the development of a red coloration of the coagulated casein

**NOTE** This reaction is dependent on the presence of tyrosin which occurs in casein to the extent of approximately 5% but has been reported in only rare instances as of curring in animal glue and gelatin and then only in doubtful traces Blood albumen and other materials give a similar test but are not usually found in papers

### PROTEINACEOUS NITROGENOUS MATERIALS IN PAPER (QUALITATIVE) <sup>82 83 84 85</sup>

A positive result obtained by the following method shall be regarded as conclusive evidence of the presence of nitrogenous (proteinaceous) materials such as glue and casein in paper This method is standardized as TAPPI T 417 m-43

**Reagent** Schmidt's Reagent—Prepare by dissolving 3 g of pure ammonium molybdate in 250 ml of distilled water and adding 25 ml of pure diluted nitric acid (2.3) This reagent is not permanent and should be freshly made at frequent intervals

**Procedure**—Boil about 0.5 g of paper for several minutes with 10 ml of a 1% solution of caustic soda (Caustic soda is necessary as the nitrogenous materials may have been made insoluble in water by hardening treatment with formaldehyde or other agents) Filter off the aqueous extract and after cooling add a suitable indicator, such as phenolphthalein then exactly neutralize with hydrochloric acid Add 1 volume of Schmidt's reagent to 2 volumes of the aqueous

<sup>82</sup> Carson F. T. Paper Trade J. 78, 168 April 10 1924

<sup>83</sup> Griffin R. C. Technical Methods of Analysis McGraw Hill New York 1927

<sup>84</sup> Chem. Z. 36, 313 1912

<sup>85</sup> Schmidt Farber Z. 24, 97 1913



extract. A white precipitate shows the presence of nitrogenous materials derived from proteins.

NOTE.—This test is very delicate. If no precipitate or only a slight precipitate is obtained, there can be no appreciable amount of proteinaceous materials present.

## STARCH IN PAPER

This standard describes procedures for the qualitative and the quantitative determination of starch in paper. It is standardized as ASTM D591-42 and TAPPI T 419 m-60.

### QUALITATIVE

**Reagent.** Iodine Solution, 0.001 *N*  $I_2$ .—Make a 0.01 *N* stock solution of iodine by dissolving 0.13 g.  $I_2$  in a solution of 2.6 g. of potassium iodide in 5 ml. of water and diluting to 100 ml. Dilute a portion of this to a pale yellow color (about 0.001 *N*) each time a test for starch is made.

**Procedure.**—A positive result obtained by the following procedure is conclusive evidence of the presence of starch in paper: boil about 0.5 g. of the paper specimen for several minutes with 10 ml. of water. Filter, cool the filtrate, and add 1 drop of the approximately 0.001 *N*  $I_2$  solution. A blue coloration indicates starch. A faint violet coloration should be disregarded, as nonstarch constituents of paper sometimes give such a reaction.

### QUANTITATIVE

This method is a colorimetric one.<sup>86</sup> The results are not seriously affected by other polysaccharides that are present in ordinary papermaking pulps. After extraction with water and hydrochloric acid, the starch is determined by measuring the absorbance of the starch-iodine complex at 580 to 610  $\mu$ . A limitation in the accuracy of the method is differences in color produced with different types of starch. This has been investigated to some extent.<sup>87</sup>

**Apparatus.** Disintegrator.—To be used for disintegrating the specimen in water. A domestic high-speed electric mixer is most suitable for this purpose. Any other means for preparing the specimens, e.g., glass beads and bottle, may be used.

**Fritted Glass Filters.**—These should be coarse, about 50 ml. or larger, to allow rapid filtration of the hydrochloric acid solutions during the extraction of the starch from the paper.

**Centrifuge.**—Preferably with a capacity of over 50 ml.

**Spectrophotometer.**—For absorption measurements at 580 to 610  $m\mu$ .

NOTE.—A filter comparator may be used, especially for a sample in which the type of starch used is unknown. In any case, use the same instrument and conditions for the calibration curve as for the specimen.

**Suction Flask.**—500 ml. or larger, with its suction line provided with a three-way cock and connections so that when its suction is cut off, a slight back pressure can be applied to the flask by blowing through the tube attached to the three-way cock.

<sup>86</sup> Browning, B. L., Bublitz, L. O., and Baker, P. S., Tappi, 35, 418, 1952.

<sup>87</sup> Harvey, J. L., Forshee, B. W., and Fletcher, D. G., Tappi, 42, 878, 1959.

Other Equipment—20 100 and 500 ml volumetric flasks 25 and 25 ml pipets and a boiling water or steam bath

Reagents Hydrochloric Acid—Concentrated HCl also solutions diluted 1:1 and 1:10

Potassium Iodide Iodine Reagent—7.5 g KI and 5 g  $I_2$  per liter Dissolve 5 g  $I_2$  in a solution of 7.5 g of KI in 10 ml of water and dilute to 1 liter

Cotton Loters

Test Specimen—From a representative sample of the paper weigh to the nearest 5 mg a 1 g specimen for the starch determination consisting of small strips. At the same time unless the moisture content is known to within 1% weigh another 1 or 2 g specimen for a moisture determination according to TAPPI Standard T 412 or T 484 m

NOTE Do not dry grind the paper since papers containing mineral filler may lose some of the filler and may also lose starch

Procedure—Transfer the specimen cut into small pieces to the disintegrator or disintegrate in a small quantity ( $60 \pm 20$  ml) of distilled water transfer quantitatively to a 250 ml beaker using enough rinsing water to make the specimen up to 100 ml Heat on the bath to just below the boiling point for 15 minutes

Transfer the contents of the beaker to the suction crucible on the suction flask. Drain and wash the residue with 10 to 12 ml of hot water Turn the three-way cock in the suction line so as to cut off the suction and connect the flask with the tube Blow gently in the tube so as to create a slight back pressure in the flask then turn the cock to seal it Add 25 ml of the 1:1 HCl to the filter crucible allow to stand for 175 to 180 seconds and apply the suction Reestablish the back pressure in the flask and repeat the 3 minute extraction with 25 ml of the 1:1 HCl Drain and reestablish the back pressure add 25 ml of concentrated HCl and allow to stand for 19 to 20 seconds Reapply the suction and turn the flask so as to mix the concentrated HCl in the filtrate Wash the residue with about 200 ml of hot water and test for complete removal of the starch by adding a drop or two of the dilute iodine solution Even a trace of residual starch will cause the appearance of a blue color

NOTE—The fritted glass filters may be cleaned by passing 5% NaOH through the filter and washing at once with hot water

Transfer the starch solution to a 500 ml volumetric flask cool to room temperature and dilute to the mark with water Mix thoroughly and if the solution is turbid because of fillers or other extraneous material centrifuge approximately 50 ml for 10 minutes

Pipet 25 ml of the clear supernatant liquid into a 50-ml volumetric flask pipet 25 ml of the  $KI I_2$  reagent into the flask dilute to the mark with water and mix thoroughly Measure the absorbance at 580 m $\mu$  against a reference solution prepared by diluting 25 ml of 1:10 HCl and 25 ml of the  $KI I_2$  reagent to 50 ml in a volumetric flask. Read the starch concentration from a calibration curve and calculate the starch content as a percentage of the oven dry paper<sup>88</sup>

<sup>88</sup> As many centrifuges do not have a capacity of 50 ml a different dilution procedure may be necessary A convenient procedure is to add an equal volume of diluted  $KI I_2$  solution containing 0.75 g and 0.5 g  $I_2$  per liter (10 ml reagent B diluted to 100 ml in a volumetric flask) to the available centrifuged starch solution and measure the absorbance against the reference solution prepared in the same way

**Calibration Curve.**—If possible, use the same starch that was added to the paper for preparing the calibration curve. Otherwise, use a composite mixture of three or four common types of starches. Weigh 0.1 g. starch corrected for moisture and ash into a 250-ml. beaker, add 100 ml. distilled water and heat for 15 minutes just below the boiling point. Add 1.0 g. cotton linters to the solution and heat 15 minutes longer. Decant with suction through the coarse fritted glass filter, wash once with hot water and refilter the water through the mat.

Proceed with the HCl and extraction treatments exactly as described for the paper specimen, diluting the filtrate to 500 ml. in a volumetric flask. Centrifuge a portion of this starch solution for 10 minutes and remove aliquots to prepare the calibration curve. Keep all the concentrations and the period between forming the starch-iodine complex and measuring its absorbance the same as used for the specimen. A suggested dilution schedule is given below.<sup>89</sup>

#### DILUTION PROCEDURE FOR PREPARING A CALIBRATION CURVE

<i>Starch Concen- tration, mg./l.</i>	<i>Total Volume, ml.</i>	<i>0.2 g./l Starch Solution, ml.</i>	<i>Water,<sup>a</sup> ml.</i>	<i>KI Solution,<sup>b</sup> ml.</i>
10	100	5	0	5
20	100	10	5	5
30	100	15	10	5
40	100	20	15	5
50	100	25	20	5

Dilute to the mark in a volumetric flask with 1:1 HCl.

<sup>a</sup> Graduated cylinder is sufficiently accurate.

<sup>b</sup> Add this solution from a pipet or buret.

**Report.**—Report the amount of starch as a percentage of the moisture-free paper to the nearest 0.1.<sup>90</sup>

**Precision.**—The standard deviation from a limited number of tests with different starches, using the added starch for calibrating, was about 0.06% starch.

**Additional Information.**<sup>91</sup>—Although a limited number of experiments indicates that centrifuging has no measurable effect on the results, it is suggested that data be obtained with and without centrifuging until this is clearly established.

This revision is comprehensive and substitutes a colorimetric starch-iodine procedure for the previous enzymatic conversion of the starch to glucose and the determination of the latter with Fehling's solution.

<sup>89</sup> The ash content of starch can usually be neglected. Acid-modified starches, oxidized starches and starches containing borax may contain 1 or 2% ash.

<sup>90</sup> In accordance with experimental findings of Harvey, Forshee, and Fletcher, the percentage of starch added to wood pulp papers is usually less than that found by this method, the relationship being approximately: % actual starch = (% starch found  $\times$  1.2 - 0.3). State prominently in the report if this correction is made.

<sup>91</sup> Since this method was approved, it has been suggested by the Verein der Zellstoff und Papier Chemiker und Ingenieure that the chemical composition of the starches used and their subsequent oxidation, have such a marked effect on the color of the starch-iodine complex as to make the accuracy of this method questionable when unknown samples are analyzed. The "diaferman" method, described by Freezer in *Die Stärke*, 10, 38, 1958, is recommended instead. This will receive attention for a subsequent revision.

## QUALITATIVE ANALYSIS OF MINERAL FILLER AND MINERAL COATING OF PAPER

This method is for the qualitative analysis of mineral constituents of filled and coated papers. The presence of such mineral matter is indicated by the amount and appearance of the ash. If the ash content is not much over 1% and the ash is light and fluffy in character added mineral filler is probably absent. If more than 1% and the ash is dense and compact added filler is likely unless waste papers have been used in the furnish; this at times may be determined microscopically.

The procedure described is generally satisfactory for determining the kind or kinds of filler used but occasionally in a borderline case a quantitative analysis may be necessary. The presence of some fillers may be determined directly by microscopic analysis.

In order to interpret qualitative ash tests with greater assurance it is important to estimate the relative amounts of the various constituents found. In this connection for example the light voluminous character of an aluminum hydroxide precipitate should be taken into account when relating its quantity to that of a heavy dense precipitate like barium sulfate. With flame and colorimetric tests it is particularly difficult to judge the relative quantities of the constituents present and these should be interpreted with special care.

The percentage of ash present may be determined in accordance with T 413 m p 1806 and the residue so obtained used for analysis. This method is standardized as ASTM D686 and TAPPI T 421 os 61.

**Reagents** Hydrochloric Acid—Concentrated HCl (sp gr 1.19) also approximately 2N (15 ml concentrated HCl diluted to 100 ml).

**Sulfuric Acid**—Concentrated  $\text{H}_2\text{SO}_4$  also approximately 5% (3 ml concentrated  $\text{H}_2\text{SO}_4$  diluted to 100 ml).

**Cobalt Nitrate Solution, 5%**—Dissolve 8 g of  $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  in 100 ml of water.

**Hydrogen Peroxide**—30%  $\text{H}_2\text{O}_2$  or a solution of 3% USP  $\text{H}_2\text{O}_2$  used in proportionately greater quantities.

**Lead Acetate Paper**—Immerse strips of filter paper in a saturated solution of  $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot 3\text{H}_2\text{O}$ .

**Lime Water, Saturated Solution**—Dissolve about 0.2 g of  $\text{Ca}(\text{OH})_2$  in 100 ml of water and filter.

**Magnesium Reagent**—Dissolve 0.5 g of *p*-nitrobenzeneazoresorcinol in 100 ml of 1% NaOH solution.

**Microcosmic Salt Solution**—Dissolve 5 g of  $\text{NaNH}_4\text{HPO}_4$  in water and dilute to 100 ml.

**Ammonium Sulfate,  $(\text{NH}_4)_2\text{SO}_4$ , Crystals**

**Sodium Carbonate,  $\text{Na}_2\text{CO}_3$ , Powdered**

**Other Reagents**—Acetic acid  $\text{CH}_3\text{COOH}$  (sp gr 1.05) ammonia concentrated  $\text{NH}_4\text{OH}$  ammonium chloride 10% solution  $\text{NH}_4\text{Cl}$  ammonium oxalate 35% solution  $(\text{NH}_4)_2\text{C}_2\text{O}_4 \cdot \text{H}_2\text{O}$  barium chloride 10% solution  $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$  potassium dichromate 4% solution  $\text{K}_2\text{Fe}(\text{CN})_6 \cdot 3\text{H}_2\text{O}$  sodium hydroxide 10% solution  $\text{NaOH}$   $\text{h}_4\text{Fe}(\text{CN})_6 \cdot 3\text{H}_2\text{O}$  sodium hydroxide 10% solution  $\text{NaOH}$ .

**Apparatus** Platinum Crucible

Charcoal Black and Blowpipe

**Platinum Wire Needle.**

**Test Specimen.**—Select sufficient paper, representative of the sample, to yield approximately 0.15 g. of ash. Ash at a temperature of about 600°C. Retain portions of the original paper for testing for sulfites, sulfides, and carbonates since these are altered in composition by ashing. If the paper is coated and separate analyses of filling materials and coating minerals are desired, remove the coating by the procedure described in T 407 m, p. 1799. Evaporate the aqueous mixture containing the coating minerals to dryness and ash the residue. Also ash the base stock and analyze these two portions separately.

**NOTE.**—If synthetic coating adhesives are used in place of starch or casein, enzymatic stripping will not work. In this case, scrape the coating off the surface with a razor blade.

**Procedure.**—An outline scheme of the complete procedure is given in Fig. 38-22.

(1) **Sulfite, Sulfide and Carbonate.**—Treat a portion of the unignited coating or paper sample in a small beaker or test tube with 2N HCl. Note whether effervescence takes place and the odor, if any, of the escaping gas.  $\text{SO}_2$  and  $\text{H}_2\text{S}$  indicate sulfites and sulfides, respectively. Warm the contents of the beaker and test the vapor with moistened lead acetate paper. The development of a metallic gray or black color confirms the presence of sulfide. In the absence of sulfides, add either a small crystal of potassium dichromate or a few drops of a 4% solution to a small portion of the HCl solution. A green coloration indicates a reducing agent; in this case probably a sulfite.

**NOTE.**—As far as is known, mixtures of sulfites and sulfides are not used in loading or coating paper.

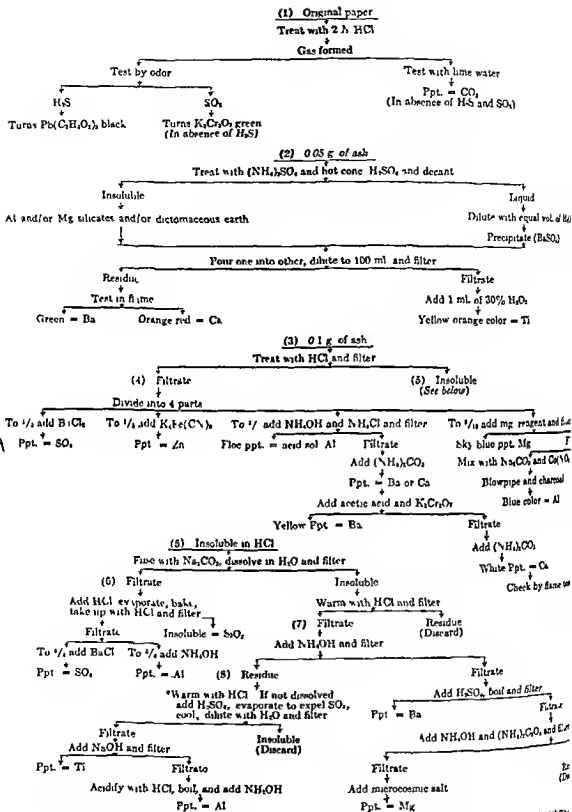
If sulfites and sulfides are absent, effervescence alone is a good indication of the presence of a carbonate, which may be confirmed by holding a glass rod with a drop of saturated lime water just above the solution. A cloudy precipitate indicates the presence of  $\text{CO}_2$ . This precipitate may later dissolve. A confirmatory test for  $\text{CO}_2$  in the presence of sulfites is to add to the contents of the beaker, a weak solution of iodine (about 0.1N) drop by drop until the entire liquid is colored yellow to oxidize the sulfites to sulfates. Then test with lime water on a glass rod as described.

(2) **Al or Mg Silicates, Ca or Ba Sulfates,  $\text{TiO}_2$ .**—To approximately 0.05 g. of ash add 10 g. of  $(\text{NH}_4)_2\text{SO}_4$  and 20 ml. of concentrated  $\text{H}_2\text{SO}_4$ . Cover with a watch glass and boil vigorously for at least 3 minutes.

Considerable undissolved matter indicates the presence of aluminum and/or magnesium silicates and/or diatomaceous earth. If the hot solution is clear, aluminum or magnesium silicates and diatomaceous earth are absent. (Calcium and barium sulfates will be dissolved unless the specimen being tested weighs much more than 0.05 g.)

Decant some of the liquid portion, cool, and dilute it cautiously with a portion (up to about five times its volume) of cold water. The formation of a precipitate on dilution, indicates the presence of barium sulfate, which is relatively soluble in hot concentrated  $\text{H}_2\text{SO}_4$ .

Mix the diluted mixture with the remainder of the undiluted mixture from the concentrated  $\text{H}_2\text{SO}_4$  treatment and add sufficient water to make the ratio of  $\text{H}_2\text{O}$  to  $\text{H}_2\text{SO}_4$  about 5 to 1. (If the original  $\text{H}_2\text{SO}_4$  solution was clear, dilute it 5 to 1 by adding water cautiously after cooling.) Filter out any residue, and to the cooled solution add 1 ml. of 30%  $\text{H}_2\text{O}_2$ . A deep yellow or orange color indicates



\* This procedure is necessary only if both Ti and HCl-insoluble Al compounds are present and it is necessary to estimate amounts of Ti and Al

FIG 38 22 Qualitative Analysis of Mineral Coating and Filler

the presence of titanium, the depth of color being proportional to the amount present. If only a very light yellow color is produced, it may be caused by  $\text{TiO}_2$  from clay, if present, or derived from  $\text{TiO}_2$  in the mill water.

The presence of barium or calcium in any insoluble residue can be determined by a flame test. Filter the solution, wash the residue with 5%  $\text{H}_2\text{SO}_4$ , dip a clean platinum wire into the moist residue, and hold it in a Bunsen flame. A green flame indicates the presence of barium, a red flame indicates calcium, and a yellow to colorless flame indicates aluminum or magnesium silicates, or both.

NOTE.— $\text{CaSO}_4$  is quite soluble in dilute  $\text{H}_2\text{SO}_4$  and may not be observed at this step.

(3) Sulfide, Sulfite, and Carbonate.—Treat 0.1 g. of the ash with 10 ml. of water and 5 ml. of concentrated  $\text{HCl}$ . Effervescence, as with step (1), indicates the presence of a carbonate or sulfite. Withdraw 1 or 2 ml. of the solution and add two drops of 4%  $\text{K}_2\text{Cr}_2\text{O}_7$  solution. A green coloration indicates sulfite.

Heat the contents of the beaker to boiling and test the fumes with moistened lead acetate paper; the development of a metallic gray or black color indicates the presence of sulfides. These tests should be checked by tests made on the original specimen of paper since carbonates may be lost, sulfates may be reduced to sulfites or sulfides or sulfites oxidized to sulfates, depending on the temperature and oxidizing conditions during ignition.

NOTE.—If the temperature of ashing is over  $900^\circ\text{C}$ . as specified in T 413 m, no carbonates will be present and any sulfites probably would be oxidized to sulfates.

Boil the mixture for at least 5 minutes unless complete solution occurs sooner. Add 35 ml. of water, and again heat to boiling. If this solution is not clear, filter and wash twice with water, reserving the filtrate for analysis of the acid-soluble portion. Wash the insoluble residue thoroughly and discard the washings. Reserve the acid-insoluble portion for later treatments (4) and (5).

(4) Sulfate, Zn, Mg, Al, Ba, Ca.—To one-fifth of the acid-soluble portion from (3) add 1 ml. of  $\text{BaCl}_2$  solution. A precipitate that appears immediately or after heating for 10 minutes, shows the presence of sulfates. To another one-fifth portion add a few milliliters of potassium ferrocyanide solution. A heavy white precipitate indicates the presence of zinc. The presence of zinc may be confirmed by the red color produced in the caustic soda-dithizone test.

To a small portion of the other three-fifths of the solution (about one-tenth of the total) add one or two drops of the magnesium reagent and make alkaline with  $\text{NaOH}$  solution; a sky-blue precipitate indicates the presence of magnesium but all other minerals commonly used in paper give a violet coloration to the solution. Take care not to add an excess of the reagent, since it is liable to mask the blue precipitate. If in doubt, filter the solution and examine the filter paper for the presence of a blue precipitate.

Mix the solution with an excess of  $\text{Na}_2\text{CO}_3$  on a charcoal block, and moisten with a very small amount of  $\text{Co}(\text{NO}_3)_2$  solution. A permanent blue coloration upon heating with a blowpipe flame confirms the presence of aluminum. (Take care not to mask the blue coloration by using an excess of cobalt nitrate solution.)

To the remainder of the solution add an excess of  $\text{NH}_4\text{OH}$  and  $\text{NH}_4\text{Cl}$  solutions. Aluminum will appear as a white floc if it is present in acid-soluble form. Filter and add  $(\text{NH}_4)_2\text{CO}_3$  solution to the filtrate. A white precipitate indicates the presence of barium and calcium. Without filtering, make the solution acid with acetic acid (which dissolves the precipitate) and add  $\text{K}_2\text{Cr}_2\text{O}_7$  solution. If barium

is present in an acid soluble form a yellow precipitate will show its presence. Filter and add an excess of  $(\text{NH}_4)_2\text{CO}_3$  solution. Since barium is removed by the preceding step a white precipitate indicates calcium. Check the precipitate for calcium by a flame test.

(5) Silicate, Sulfate, Al.—Place the unfolded filter paper containing the remainder of the acid insoluble portion from (3) in a platinum crucible. Dry and ignite with free access of air until all organic matter is removed. Add 1 to 2 g of  $\text{Na}_2\text{CO}_3$  and fuse until a clear melt is obtained or until all reaction has ceased. Decompose the melt in 25 ml of hot water heat to boiling filter and wash the paper thoroughly with water. Reserve the filtrate and the first two washings for the analyses of the water soluble portion for silicate and aluminum.

Wash the insoluble portion from the filter paper back into the original beaker with a stream of water place the beaker under the funnel and pour 10 ml of hot concentrated HCl through the filter paper. Reserve the contents of the beaker for analysis of the water insoluble portion according to section (6).

Make the water soluble portion slightly acid with HCl evaporate to dryness in the platinum dish and bake at  $150^\circ \pm 5^\circ\text{C}$  for  $\frac{1}{2}$  to 1 hour. Moisten the residue with concentrated HCl let stand a few minutes then add 5 to 10 ml of dilute HCl and warm. A light flocculent insoluble residue in the solution indicates the presence of silicate which is best observed by viewing against a dark background. Filter and to one fourth of the filtrate add  $\text{BaCl}_2$  solution a precipitate indicates sulfates. To the remainder of the filtrate add  $\text{NH}_4\text{OH}$ . A precipitate indicates aluminum.

(6) Al Fe Ba Mg.—Warm the acid solution of the water insoluble portion from (5) until no more material dissolves add 50 ml of water boil and add a very slight excess of  $\text{NH}_4\text{OH}$  to precipitate aluminum (and iron). Filter and wash reserve the precipitate for analysis according to (7) below. To the filtrate add 5 ml of 5%  $\text{H}_2\text{SO}_4$  to precipitate barium boil and filter. Make the filtrate ammoniacal add a little ammonium oxalate solution to insure the absence of calcium filtering if any precipitate appears then add to the cold solution 5 ml of  $\text{NH}_4\text{OH}$  an excess of microcosmic salt solution and stir well. A precipitate appearing in 15 minutes will indicate the presence of magnesium compounds.

(7) Ti and Al.—The following procedure is necessary only if both titanium and HCl insoluble aluminum compounds are present and it is desired to estimate the relative proportions of titanium and aluminum. Wash the insoluble precipitate obtained by addition of  $\text{NH}_4\text{OH}$  in (6) with water and then transfer it to the original beaker with a stream of water. Add 5 ml of concentrated HCl and warm. If solution is not complete add 3 ml of concentrated  $\text{H}_2\text{SO}_4$  and heat until solution occurs, then drive off the  $\text{SO}_3$  fumes over a free flame under a hood. Cool and dilute to 35 ml. Any  $\text{BaSO}_4$  not decomposed by the  $\text{Na}_2\text{CO}_3$  fusion will be insoluble at this point and should be removed by filtration. Make the solution neutral with 10% NaOH and add an additional volume equal to that of the neutralized solution. Heat to boiling cool and filter. Titanium hydroxide remains insoluble. Neutralize the filtrate with HCl heat to boiling and make slightly ammoniacal. If any precipitate forms it is  $\text{Al}(\text{OH})_3$ .

Report.—Report all cations anions and radicals found and indicate their relative amounts present such as trace slight amount considerable large amount etc. It is desirable also to interpret and report results of the analysis in terms of the fillers or mineral coating materials indicated to be present.



**Interpretation of Results.**—For the fillers listed, positive tests will be obtained in the procedural sections indicated. See also Additional Information, below.

Calcium carbonate—Ca (4), CO<sub>2</sub> (1).  
 Calcium carbonate with magnesium hydroxide or carbonate—Ca (4), Mg (4), CO<sub>2</sub> (1).  
 Calcium sulfate—Ca (4), SO<sub>4</sub> (4).  
 Calcium sulfite—Ca (4), SO<sub>2</sub> (1).  
 Barium carbonate—Ba (4), CO<sub>2</sub> (1).  
 Barium sulfate—Ba (6), SO<sub>4</sub> (5).  
 Lithopone—Sulfide (1), Zn (4), Ba (6), SO<sub>4</sub> (5).  
 Zinc oxide—Zn (4).  
 Zinc sulfide—Zn (4), Sulfide (1).  
 Titanium dioxide—Ti (2), or (7).  
 Titanium dioxide-barium sulfate—Ti (2) or (7), Ba (6), SO<sub>4</sub> (5).  
 Titanium dioxide-calcium sulfate—Ti (2) or (7), Ca (4), SO<sub>4</sub> (4).  
 Satin white (coating)—Al (4), Ca (4), SO<sub>4</sub> (4), CO<sub>2</sub> (1).  
 Clay—Al (5) and (7), SiO<sub>2</sub> (5).  
 Talc or asbestine—Mg (6), SiO<sub>2</sub> (5).  
 Diatomaceous earth—SiO<sub>2</sub> (5).

**Additional Information.**—The analysis can be considerably simplified if it is desired only to establish the presence or absence of a particular filler.

The use of sulfides as filling or coating materials in the paper industry is restricted to ZnS alone or in combination with BaSO<sub>4</sub> (lithopone). A positive test for Zn in the absence of sulfide indicates the use of ZnO in the paper. A combination of the oxide and sulfide cannot be identified as such. The amount of zinc pigments in paper can be determined by TAPPI Standard T 438 m. The use of sulfites is restricted to calcium sulfite.

Most commercial fillers contain impurities that may lead to incorrect conclusions if only small amounts or traces of constituents are found. For example, satin white may contain carbonate; clays, especially domestic clays, contain a small quantity of titanium and clays may also contain calcium and magnesium; titanium dioxide may contain small amounts of aluminum and sulfate; calcium fillers may contain magnesium; sulfide and sulfite fillers usually contain sulfates.

The common use of alum in papermaking leads to the presence of aluminum compounds in appreciable quantities, even when fillers are absent. Small quantities or traces of calcium, magnesium sulfates, etc., are observed in many papers containing no filler and are derived from the mineral constituents of the pulp or left in the paper before drying, particularly from a mill in which the water is hard.

Carbonates together with considerable acid-soluble calcium indicate the presence of calcium carbonate which may exist as chalk or whiting. If HCl-soluble magnesium is also present, a mixture of calcium and magnesium carbonates is indicated. A combination of barium and carbonate may exist as witherite. Barium in this form will be shown in the HCl-treated portion of the ash since barium sulfate is insoluble in dilute HCl.

A positive test for acid-soluble sulfates and calcium indicates the use of calcium sulfate as crown filler, gypsum, satin white, etc. If considerable HCl-soluble aluminum is also present in the coating, the mineral used may be satin white. If carbonates are used in conjunction with sulfides, there may be a positive test for sulfates when none are present.

A positive test for calcium and sulfite indicates the presence of calcium sulfite.

The presence of considerable magnesium and silicate indicates the use of talc, agalite, or asbestine. Silica may also indicate the presence of diatomaceous earth.

The characteristic diatom forms may be readily recognized on microscopic examination.

The residue from the portion of the ash treated with concentrated  $H_2SO_4$  may be clay, talc, diatomaceous earth, or a mixture of these substances. A positive test for aluminum indicates that clay was used.

Barium sulfate (barytes or blanc fixe) is indicated by the formation of a precipitate on the dilution of the  $H_2SO_4$  solution and by a positive flame test for barium on the residue.

Titanium may be present as titanium dioxide alone or mixed with barium or calcium sulfates. Titanium-barium mixtures are not likely to be found in paper made in North America, but titanium-calcium mixtures may be found in papers made in America and abroad.

Any of these may be used in conjunction with other fillers—for example, with clay. The quantitative determination of titanium pigments in paper is given in TAPPI Standard T 439 m.

A microscopic examination of the ash (see T 488 sm) usually proves to be a useful adjunct to chemical analysis and if possible should be attempted.

### WATER-SOLUBLE ACIDITY OR ALKALINITY OF PAPER

This method is not applicable to highly alkaline papers such as those containing casein or calcium carbonate. This method is standardized as ASTM D 4841 and TAPPI T 428 m 45.

**Apparatus**—The special apparatus required for this test is a grinder which will completely disintegrate the paper without heating or contaminating it and a steam or oil bath which can be maintained at  $100^\circ C$ . The grinder shall be a hoerner type or its equivalent.

The balance used for weighing shall be sensitive to 1 mg.

The glassware shall be acid and alkali resistant.

**Reagents** Sodium Hydroxide Solution, 0.01 *N*—Conveniently made by diluting 100 ml of 0.1 *N* NaOH to 1 liter with freshly boiled and cooled distilled water.

Hydrochloric or Sulfuric Acid, 0.01 *N*.

Phenolphthalein Indicator Solution.

**Test Specimen**—The specimen for test shall be cut from the test sample in such a way as to be thoroughly representative of it and shall be completely disintegrated in the grinder.

**Procedure**—Allow the ground specimen to come to moisture equilibrium with the atmosphere of the balance case and weigh at the same time 5 g portions (to nearest 1 mg) for the acid extractions and moisture determination. Determine the moisture content on one portion by ASTM Standard D 644 55 (p. 1804). Transfer another weighed portion to a 500 ml Erlenmeyer flask and add 250 ml of boiling water. In some cases, the fibers absorb water slowly and tend to float on the surface of the water. This is avoided by first adding small portions of the water and shaking well until the fibers are thoroughly saturated. After the water is added affix to the flask a stopper containing a narrow glass tube about 30 in. in length which serves as a condenser. A soil digestion flask which has a ground glass stopper and condensing tube in one piece or a rubber stopper covered with metal foil may be used. Place the flask in a heating bath which will maintain the contents of the flask at 98 to  $100^\circ C$ . Heat at this temperature for 1 hour with occasional shaking. At the end of this period pour the contents of the flask on a Buchner

funnel (without other filtering medium) and wash the fibers remaining in the flask into the Büchner funnel with 10 ml. of water. Apply strong suction to the fibers, then cool the extract rapidly and titrate it as soon as it reaches room temperature. Add phenolphthalein indicator and if the extract remains colorless, determine the acidity by titrating with 0.01 *N* NaOH until the first appearance of a permanent pink coloration. If on addition of phenolphthalein, the extract has a pink color, determine the alkalinity by titrating with 0.01 *N* HCl or H<sub>2</sub>SO<sub>4</sub> until the color is just discharged. Make a blank titration on 250 ml. of the water heated for 1 hour in the same bath and with the same glassware used for the extractions.

Each test result used in calculating the acidity or alkalinity shall be the average of not less than two determinations. The percentage results of duplicate determinations shall agree within 0.01.

Report.—Total acidity or alkalinity shall be expressed as a percentage of the moisture-free paper in terms, respectively, of sulfuric anhydride, SO<sub>3</sub>, or in terms of sodium oxide, Na<sub>2</sub>O, to the nearest 0.01. They are calculated as follows:

Let  $T_1$  = ml. NaOH required to neutralize extract,  
 $T_2$  = ml. acid required to neutralize extract,  
 $t$  = ml. of NaOH required to neutralize the blank,  
 $N_1$  = normality of NaOH solution,  
 $N_2$  = normality of acid solution,  
 and  $W$  = weight of test specimen less moisture.

$$\text{Then (1) per cent SO}_3 = \frac{(T_1 - t) \times N_1 \times 0.04 \times 100}{W},$$

$$\text{or (2) per cent Na}_2\text{O} = \frac{(T_2 \times N_2 + t \times N_1) \times 0.03 \times 100}{W}.$$

**Additional Information.**—This method is based on the method for acidity described by S. Kohler and G. Hall in *The Paper Industry* 7, No. 7 (Oct. 1925), with some modifications developed at the National Bureau of Standards. In this revised method, one extraction is specified instead of the three extractions originally specified, because Kohler subsequently found that one extraction is sufficient for classification of paper. In "Investigation into the Determination of Acidity and Copper Number in Paper, Statens Provingsanstalt," Stockholm, Meddelande 56, 1932, it is stated that the acid number thus obtained is about  $\frac{3}{4}$  of that obtained by three extractions.

Studies of this method and other acidity methods are reported by Wehmhoff and by Wehmer in *Technical Association Papers* (TAPPI), May, 1930, and May, 1931.

The Koerner type of grinder is described in National Bureau of Standards *Research Paper* RP295.

## ALPHA-, BETA-, AND GAMMA-CELLULOSE IN PAPER

Cellulose consists analytically of three fractions, alpha, beta, and gamma. In this method the alpha-fraction is the cellulose which can be filtered out of a mixture consisting of the fibrous material and 7.3% sodium hydroxide solution of maximum dissolving power, after the fibers have previously been swollen with 17.5% sodium hydroxide solution. The beta-cellulose is taken as that fraction which precipitates at room temperature (15 to 35°C.) after the filtrate has been acidified, whereas the

gamma fraction remains in solution. After separation the alpha cellulose is determined either by drying and weighing or volumetrically by oxidation with bichromate. Both methods for alpha cellulose are capable of the same reproducibility and give practically the same values. In the volumetric method no moisture or ash determinations are made and a much smaller sample is used, resulting in a shorter and more rapid procedure. For beta and gamma cellulose, only the volumetric method is practicable.

The method of separating the alpha from the other two fractions is intended primarily for papers made from rags or chemical wood fibers. If the analyst desires information as to the applicability of the method to papers containing large amounts of lignin such as newsprint, he is referred to the original literature<sup>92</sup> for details of technique. This method is standardized as ASTM D588-42 and TAPPI T 429 m-48.

**Apparatus.**—The special apparatus required for this test is

A disintegrator which will completely disintegrate the paper without heating or contaminating it. A Koerner type or its equivalent shall be used. This is described in the literature.<sup>93</sup>

A device with which uniform mixture of the ground material can be secured. A mixer is easily constructed by fitting a crock or bell jar, of approximately equal diameter and depth, with a wooden lid, through which runs the shaft of an electric fan, vanes being properly placed to produce turbulence. Twenty to forty seconds at full speed normally suffice; longer periods result in separation of the light material from the heavy.

A water bath which can be maintained at  $20.0 \pm 0.1^\circ\text{C}$ .

For the determination of bichromate, an indicator may be used as described below, but for rapid accurate analysis electrometric apparatus is recommended. An ordinary potentiometric circuit with a platinum wire electrode and crude calomel half cell is suitable. More simply, a nichrome wire may be substituted for the calomel cell. The nichrome wire is prepared for use by heating momentarily to bright redness and then scraping the surface clean with a knife. The potentiometric arrangement may consist of a galvanometer with a sensitivity of 0.5 to 1 microamp per mm scale division, a dry cell, and a sliding contact rheostat having a total resistance of approximately 400 ohms. Smaller rheostats will suffice but they drain the dry cell more quickly. The simplest form of the apparatus is shown in Fig. 38-23. The large deflection at the end point is unmistakable from possible slow creeping during the titration. The galvanometer is adjusted to zero by varying the resistance at the beginning of the titration.

**Reagents.** Sodium Hydroxide Solution, 17.5% (5.24 N).—Allow a 50% solution of  $\text{NaOH}$  to stand about 1 week in a stoppered vessel to permit settling of  $\text{Na}_2\text{CO}_3$ . Draw off 200 ml of the supernatant liquid with a pipet, add about 50 ml of distilled water and 1 ml of 1.5 M  $\text{BaCl}_2$  solution to lessen the effect of  $\text{CO}_2$  on the end point, and titrate with standard 1 N hydrochloric acid using phenolphthalein as indicator. Knowing the approximate normality of the concentrated  $\text{NaOH}$ , dilute it with distilled water to  $5.24 \pm 0.03$  N, checking the diluted  $\text{NaOH}$  by titrating 10.00 ml of it as before, and diluting further, if necessary, to obtain the normality specified, which will correspond to a strength of  $17.5 \pm 0.1\%$ .

<sup>92</sup> Launer, H. F. J. Research Natl. Bur. Standards 18, 333, March, 1937, RP979.

<sup>93</sup> Launer, H. I. Ibid., 20, 87, Jan., 1938, RP1068.

<sup>94</sup> Burton, J. D., and Rasch, R. H. Ibid., 6, 603, April, 1931, RP295.

(The final solution should have a density of  $1.194 \pm 0.001$  at  $15^{\circ}\text{C}$  or  $1.192 \pm 0.001$  at  $20^{\circ}\text{C}$ )

**Potassium Bichromate Solution.**—Dissolve 90.0 g of c.p. moisture free ( $100\text{--}105^{\circ}\text{C}$ )  $\text{K}_2\text{Cr}_2\text{O}_7$  in hot water ( $70\text{--}90^{\circ}\text{C}$ ) and dilute to 1 liter after allowing the solution to cool

**Ferrous Ammonium Sulfate Solution.**—Dissolve 195 g of c.p.  $\text{Fe}(\text{NH}_4)_2(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$  in water containing 10 ml of concentrated  $\text{H}_2\text{SO}_4$  and dilute to 1 liter. If the solution is kept out of contact with oxygen, by a slow, continuous stream of hydrogen, for example, its strength will remain quite constant. The amount of  $\text{H}_2$  thus used is about one fifth of a 200 cu ft cylinder per year. This is not necessary, but reduces the frequency with which the bichromate/ferrous ammonium sulfate ratio must be determined from daily to two or three times monthly.

**Acetic Acid Solution** (for gravimetric procedure).—Prepare a solution of acetic acid approximately 10% by weight.

**Bichromate Indicator.**—If electrometric apparatus is not available, dissolve 0.3 g of barium diphenylaminesulfonate and 0.5 g of  $\text{Na}_2\text{SO}_4$  in 100 ml of water. Use 5 to 10 drops in a solution sufficiently dilute for good observation of the end point, which is from red to green. As an alternative, the outside indicator potassium ferricyanide solution may be placed in drops upon white porcelain. The end point occurs when a drop of the solution being titrated turns a drop of the indicator blue.

**Barium Chloride, 1.5 M.**—(For use in standardizing the 5.24 N NaOH.) Dissolve 37 g of  $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$  in water and dilute to 100 ml.

**Sulfuric Acid, 12 M.**—Cautiously add 3 volumes of c.p. concentrated  $\text{H}_2\text{SO}_4$  (sp. gr. 1.84) to 2 volumes of water. The water is contained in a Pyrex flask, cooled by tap water, and the acid is added in small portions, shaking after each addition. This acid is then approximately 72% by weight.

**Sulfuric Acid, 6 N.**—Dilute 1 volume of the 12 M sulfuric acid to 3.5 volumes in a graduated cylinder. After mixing, standardize against the 5.24 N NaOH and then add sufficient water to give a normality of  $6.0 \pm 0.1$ .

**Test Specimen.**—The test specimen shall be cut from the sample in such a way as to be thoroughly representative of it. It shall be reduced to cotton-like form in the disintegrator and then thoroughly mixed. If the paper is mineral coated, remove the coating before analysis according to the procedure described in TAPPI Standard T 407 m (p. 1799).

**Procedure for Alpha Cellulose. Volumetric Method.**<sup>92</sup>—Perform all operations (except weighing) described in the following paragraph and keep all liquids, as nearly as possible, at  $20.0 \pm 0.1^{\circ}\text{C}$ .

Weigh  $0.3 \text{ g} \pm 10 \text{ mg}$  of the specimen in a 100 ml beaker. Add 20.0 ml of

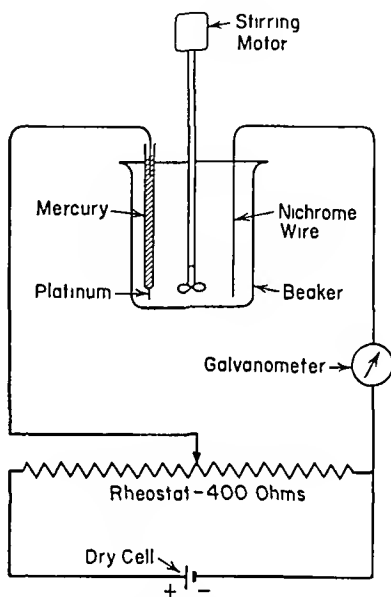


FIG 38-23 Electrometric Apparatus for Titrating Potassium Bichromate with Ferrous Ammonium Sulfate Solution

17.5% NaOH solution macerate until the fibers are uniformly wet and dispersed and let stand 10 minutes from the time of addition of NaOH. Then add 33.0 ml of water stir the mixture thoroughly and let stand 1 hour longer stirring once during the interval. After stirring once more pour about 5 ml of the unsettled mixture on an 80 mesh copper or brass wire screen fitted into a Gooch crucible. The crucible and ring are supported by a funnel fitted into the neck of a 100-ml volumetric flask with a rubber stopper through which passes a glass tube for suction. Form a mat with gentle suction (pressure differential 10 to 20 mm of  $H_2O$ ). Avoid excessive packing of the fibers as this retards filtering. It may be necessary to refilter the first filtrate but loss of small amounts of alpha cellulose to the filtrate does not affect the results appreciably. Pour the remainder of the mixture on the mat and before the last of the liquid has run through wash the beaker and the mat with 35 ml of water.

Moisten the residue of alpha cellulose with water and remove it from the crucible. Place the crucible upright in a 400 ml beaker fill it with 25 ml of 1%  $H_2SO_4$  at room temperature and rinse it after a few minutes with 50 ml more of the acid. Disintegrate the alpha cellulose pad in the acid using a thermometer as a stirring rod. Add to the alpha cellulose solution with a pipet 25.00 ml of the bichromate solution and heat at 140 to 150 C for 10 minutes. Bubble air in a fine stream through the solution to prevent bumping and keep the beaker covered with a watch glass notched to permit entrance of the thermometer and the bubble tube.

After the solution has cooled to 130 C add 50 ml of water rinse the thermometer etc and cool the solution to 60°C or lower. Titrate the remaining bichromate with the ferrous ammonium sulfate solution.

Pipet exactly half of the filtrate from the alpha cellulose after all fibers present have settled into a 400 ml beaker containing 50 ml of the bichromate solution. If the paper contains oxidizable fillers such as ZnS pigment or  $CaSO_3$  filter the filtrate once through a thick pad of asbestos in a Gooch crucible before taking the portion for analysis. (Such fillers remaining with the alpha cellulose may cause some error but this is usually slight.) Cautiously and with constant stirring pour 50 ml of concentrated  $H_2SO_4$  down the side of the beaker containing the portion of the filtrate then heat and titrate as before.

The amount of bichromate solution consumed in milliliters is calculated for each fraction as follows:

$$(A) \text{ For alpha fraction ml} = 25 - (v_1 \times r)$$

$$(B) \text{ For filtrate ml} = 2(5 - v_2 \times r)$$

where  $v_1$  and  $v_2$  represent the volumes of ferrous ammonium sulfate necessary to titrate the bichromate remaining after oxidation in the two cases respectively and  $r$  is the volume of bichromate solution equivalent to 1 ml of ferrous ammonium sulfate solution determined frequently by titrating 5 ml of bichromate solution in 100 ml of 1.1  $H_2SO_4$ . The alpha cellulose percentage of the total cellulose is calculated from the volumetric data by substitution in the following equation:

$$\text{Alpha cellulose \%} = \frac{(A) \times 100}{(A) + (B)}$$

NOTE—The original literature<sup>23</sup> should be consulted if the analyst is in doubt as to further details of these calculations.

If rosin, starch, or glue is present, the bichromate volumes are previously corrected as follows: The amounts of sizing materials remaining with the alpha-cellulose are taken as 0.25% glue, 0.2% starch, and 0.2% rosin, based on the dry weight of the paper. These are average values, but actual amounts were found to vary not more than 0.1 from them, irrespective of the content of glue, starch, or rosin in the papers.

As an example, if a paper were found to contain 3.4% glue, 0.7% starch, and 1.1% rosin, then the sizing materials reaching the beta-plus-gamma portion would be 3.15, 0.5 and 0.9%, respectively. After these values are converted into weights, they may then be converted into milliliters of the bichromate solution by dividing each weight by the corresponding bichromate factors, which are 0.0154 g. per ml. for glue, 0.0129 g. per ml. for starch, and 0.0066 g. per ml. for rosin. The resulting volumes in milliliters of the bichromate solution are subtracted from the volumes of bichromate consumed by the alpha and by the beta-plus-gamma fractions, which are then substituted in the equation given.

**Gravimetric Method.**—Allow the specimen to come to moisture equilibrium with the atmosphere of the balance. Weigh, to the nearest milligram, 1.5 g. of the specimen for the alpha-cellulose determination. Weigh at the same time samples for moisture and ash determinations, and for determinations of such other non-cellulose components as may be found necessary for calculation of the total cellulose content, such as fillers and sizing materials. Determination of the amounts of such materials shall be made according to the TAPPI standard methods.

Perform all operations and keep all liquids, as nearly as possible, at  $20.0 \pm 0.1^\circ\text{C}$ . Add 100 ml. of 17.5% NaOH solution to the sample in a 400-ml. beaker. Macerate until uniformly wet and dispersed, and let stand 10 minutes from the time of addition of NaOH. Dilute with 165 ml. of water, stir the mixture thoroughly, and let stand 1 hour longer, stirring once during the interval. After stirring once more, pour the mixture upon a medium-weight cotton cloth cut to fit a 7.5-cm. Büchner funnel, the cloth having been previously washed and the fitted piece dried to constant weight at 100 to  $105^\circ\text{C}$ . and weighed in a weighing bottle before use. Remove by refiltration any fibers passing through the filter. Before the last of the liquid has run through, add water, break up the pad well with a pointed stirring rod, and keep in a loose condition until 200 ml. of wash water have passed through. Then cover the alpha-cellulose with 10% acetic acid and allow to soak for 5 minutes, after which pass an additional 500 ml. of wash water through while breaking up the pad with the pointed stirring rod.

Dry the alpha-cellulose overnight on the cloth in the original weighing bottle at 100 to  $105^\circ\text{C}$ ., cool, and weigh it. Determine the ash content and correct the weight accordingly. The sizing materials, if any, remaining with the alpha-cellulose are taken as 0.25% glue, 0.2% starch, and 0.2% rosin, based upon the dry weight of the test specimen, and the corresponding weights subtracted from the total.

**Report for Alpha-Cellulose.**—The percentage of alpha-cellulose shall be based upon the total cellulose, including pentosans, but excluding moisture, ash, rosin, or any sizing or other added nonfibrous materials. All determinations of alpha cellulose shall be made in duplicate, the results of which shall agree within 0.4 or better, and the average shall be expressed to the nearest whole per cent. The report shall state whether the volumetric or the gravimetric method was used.

**NOTE.**—The precision of the volumetric method is much greater than these requirements would indicate. It is felt, however, that the average value of two determinations which differ by 0.4, when expressed in per cent, adequately represents the sample as

prepared for testing. When however a given sample is ground and tested in different laboratories greater disagreement may arise due to the differences in fineness and extent of fibrillation of the fibers on the one hand and individual differences in analysis on the other added to the lack of perfect uniformity of sample and ordinary errors in analysis. Therefore the reporting of alpha cellulose values to the nearest 1% is more compatible with experience and is sufficient for the practical usefulness of the value. The same remarks apply to beta and gamma cellulose values.

**Procedure for Beta and Gamma Cellulose**—Use the remainder of the filtrate from the volumetric alpha cellulose method for this determination. Acidify with 15 to 16 ml of 6 N  $\text{H}_2\text{SO}_4$  and after cooling dilute the mixture to 100 ml pour into a cylinder and let stand at room temperature until the beta cellulose has settled which is usually overnight. Then remove 50 ml of the supernatant liquid oxidize and titrate as before.

The percentage of gamma cellulose is calculated by substitution in the following equation after being corrected as previously described for any glue and starch but not rosin in the same manner as the alpha cellulose.

$$\text{Gamma cellulose } \% = \frac{(\text{ml } \text{K}_2\text{Cr}_2\text{O}_7 \text{ for gamma portion}) \times 400}{\text{ml } \text{K}_2\text{Cr}_2\text{O}_7 \text{ for alpha fraction and filtrate}}$$

The percentage of beta cellulose is calculated by subtracting the sum of the alpha and gamma percentages from 100.

**Report for Beta and Gamma Cellulose**—The basis for reporting beta and gamma cellulose is the same as that for alpha cellulose.

## TITANIUM PIGMENTS IN PAPER

This method describes procedures for a qualitative and for a volumetric and a colorimetric quantitative determination of titanium dioxide ( $\text{TiO}_2$ ) in paper. This method is standardized as T 439 m 60.

### QUALITATIVE TEST

**Reagents** Sulfuric Acid—Concentrated  $\text{H}_2\text{SO}_4$

Ammonium Sulfate  $(\text{NH}_4)_2\text{SO}_4$

Hydrogen Peroxide 3%  $\text{H}_2\text{O}_2$ , USP

**Test Specimen**—Obtain a representative specimen of the paper to yield about 0.5 g of ash.

**Procedure**—Ash the specimen at about 900°C in a clean dish or crucible. Place approximately 0.5 g of the ash in a 250 ml beaker add 20 ml of concentrated  $\text{H}_2\text{SO}_4$  10 g of  $(\text{NH}_4)_2\text{SO}_4$  and boil for at least 5 minutes. An insoluble residue indicates siliceous matter. Cool the solution, dilute to 100 ml with water and heat to boiling. Let settle and filter through double close textured ashless filter paper. To the filtrate add 5 to 10 ml of 3%  $\text{H}_2\text{O}_2$ . A clear yellow or orange color indicates the presence of titanium.

### QUANTITATIVE TESTS

Unless its composition is known it is usually desirable to make a complete qualitative analysis of the ash (see TAPPI Standard T 421 m, p 1812) to facilitate the quantitative analysis.



## VOLUMETRIC PROCEDURE

The titanium in a dilute sulfuric acid solution of the ash is reduced, then titrated with a standardized ferric ammonium sulfate solution.

**Apparatus.** Reduction Apparatus.—As shown in Fig. 38-24, it comprises a stoppered 500-ml. conical flask with a 5-mm. delivery tube leading to a 250-ml. beaker, and a glass rod extending downward from the stopper to hold a piece of aluminum foil.

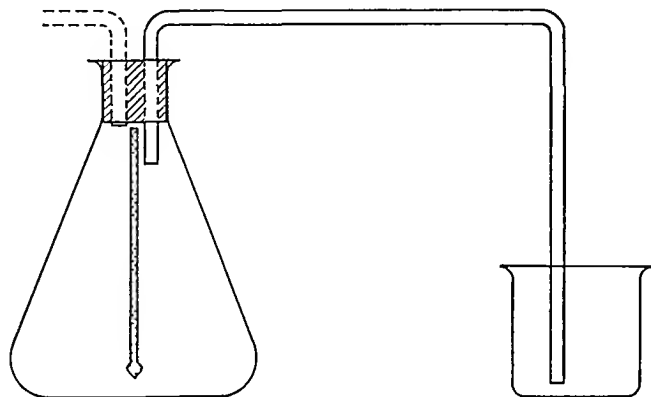


FIG. 38-24. Reduction Apparatus.

**Ashing Equipment.**—A silica, or preferably a platinum, dish and a muffle furnace at 900°C.

**Reagents.**—Ammonium Sulfate,  $(\text{NH}_4)_2\text{SO}_4$ .

**Sulfuric Acid.**—Concentrated  $\text{H}_2\text{SO}_4$ .

**Hydrochloric Acid.**—Concentrated  $\text{HCl}$ .

**Aluminum Metal Foil.**—Electrolytic grade, preferably about 0.008 in. thick.

**Standard Titanium Dioxide.**—Obtainable from the National Bureau of Standards, with analysis.

**Potassium Permanganate Solution, approximately 0.1 N.**—Dissolve 3.16 g. of  $\text{KMnO}_4$  in distilled water and dilute to 1 liter.

**Standardized Ferric Ammonium Sulfate Solution.**—Dissolve 30.16 g. of fresh  $\text{FeNH}_4(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$  in 800 ml. of distilled water containing 15 ml. of concentrated  $\text{H}_2\text{SO}_4$ . Add 0.1 N  $\text{KMnO}_4$  until a very slight pink color is obtained; dilute to exactly 1 liter, and mix well. Filter if cloudy. Standardize against the standard  $\text{TiO}_2$  solution using 0.1900 to 0.2100 g. of  $\text{TiO}_2$  and following the same procedure as for the paper ash. Calculate the solution factor as follows:

$$\text{Factor} = \frac{\text{grams NBS TiO}_2 \times \% \text{ TiO}_2 \text{ in NBS TiO}_2}{\text{milliliters of titrant} \times 100}$$

This factor should be about 0.005 g. of  $\text{TiO}_2$  per milliliter of the solution.

**Ammonium Thiocyanate Indicator.**—Dissolve 24.5 g. of  $\text{NH}_4\text{SCN}$  in 80 ml. of hot distilled water, filter, bring to room temperature, and make up to 100 ml. in a graduated cylinder with distilled water. Keep in a well-stoppered, dark-colored bottle.

**Sodium Bicarbonate Solution**—Prepare a saturated solution with distilled water at the time of analysis. About 17 g of  $\text{NaHCO}_3$  added to 150 ml of water will be required. (May be replaced with water if the carbon dioxide cylinder is used.)

**Carbon Dioxide (Optional)**—Cylinder of compressed carbon dioxide

**Test Specimen**—Weigh representative portions of the paper sufficient to give a specimen containing, as near as can be judged, about 0.15 g of  $\text{TiO}_2$ .

**Procedure**—Determine the moisture content of the paper if not known to within 1%. Ash the paper at about  $900^\circ\text{C}$  in a clean dish or crucible. Weigh the ash to obtain the percentage on the moisture free weight of the paper, then accurately weigh a portion to contain from 0.05 to not over 0.25 g of  $\text{TiO}_2$  and put into the 500 ml flask of the reduction apparatus. Usually 0.5 g of ash is sufficient.<sup>95</sup>

Add 7 to 9 g of  $(\text{NH}_4)_2\text{SO}_4$  and 20 ml of concentrated  $\text{H}_2\text{SO}_4$  to the flask. Mix well and heat on a hot plate until fumes of  $\text{SO}_3$  are evolved. Continue to heat strongly until solution is complete (usually requires not over 5 minutes of boiling) or it is apparent that the residue is composed of siliceous matter.

If the ash cannot be completely dissolved, fuse another weighed portion in a platinum crucible with 8 g of anhydrous  $\text{Na}_2\text{CO}_3$  and 1 hour at  $900^\circ\text{C}$ . Cool and place the crucible and its contents in a 250 ml beaker and add 40 ml of distilled water and 70 ml of concentrated  $\text{HCl}$ . When the specimen is dissolved, remove the crucible and its cover and evaporate the solution in the beaker to a volume of about 75 ml. If insoluble matter is present, filter through fine paper and wash with about 5 ml of distilled water.

Cool and with caution add 120 ml of distilled water and 20 ml of  $\text{HCl}$ . Bring to a boil and remove from the heat.

Insert the short end of the delivery tube into one hole of the 2 hole stopper for the 500 ml flask. Insert the glass rod having the slight hook or collar at the bottom into the other hole of the stopper as shown. Attach approximately 1 g of aluminum foil to the bottom end of the rod by coiling and crumpling it around the rod. It is usually desirable to fold the aluminum foil one or more times to reduce the rate of reaction. A dissolving period of about 5 minutes has been found satisfactory.

Push the stopper with the foil and delivery tube, into the flask and at the same time submerge the long end of the delivery tube in the 250 ml beaker containing about 200 ml of the  $\text{NaHCO}_3$  solution.

As soon as the aluminum has dissolved, gently boil the contents of the flask for 3 to 5 minutes without removing the delivery tube. Carefully cool to about  $60^\circ\text{C}$  preferably by partial immersion of the flask into a vessel of water. The  $\text{NaHCO}_3$  solution will be sucked into the flask during this cooling and with a rapid reaction will give an atmosphere of  $\text{CO}_2$  over the reduced titanium solution. Withdraw the stopper, but before removing the stopper, rod and delivery tube completely, rinse the glass rod attached to it with a little distilled water catching the rinse water in the flask. Add 2 ml. of the  $\text{NH}_4\text{SCN}$  indicator and titrate immediately with ferric ammonium sulfate to a straw colored end point. It is best to add the bulk of the ferric solution rapidly and then, after shaking, finish the titration drop by drop.<sup>96</sup>

<sup>95</sup> If only the percentage of  $\text{TiO}_2$  in the paper, and not the proportional amount of  $\text{TiO}_2$  in the ash is required, ash a weighed representative portion of the paper in a platinum crucible and transfer quantitatively to the 500 ml. flask.

<sup>96</sup> Instead of using the  $\text{CO}_2$  generated from the  $\text{Na}_2\text{CO}_3$  solution to provide the required protective atmosphere, the  $\text{CO}_2$  may be supplied from a cylinder through a connection to

Calculate the percentage of  $\text{TiO}_2$  in the moisture-free paper from the titration and the factor of the solution as follows:

$$\% \text{ TiO}_2 = \frac{\text{milliliters of titrant} \times \text{factor} \times 100}{\text{weight of specimen in grams}}$$

The result will include chromium, antimony, and any other substance which is reduced by the aluminum and subsequently oxidized by ferric ions. However, appreciable quantities of interfering materials are usually not likely to be encountered in paper ash.

### COLORIMETRIC PROCEDURE

The titanium in dilute  $\text{H}_2\text{SO}_4$  solution is combined with  $\text{H}_2\text{O}_2$  and the resulting yellow to brownish orange complex, is measured spectrophotometrically. Use this procedure when the amount of  $\text{TiO}_2$  in the ash conveniently available, is less than 0.01 g., or when the paper has a high filler content other than  $\text{TiO}_2$ .

**Apparatus.** Spectrophotometer.—A spectrophotometer or other instrument for accurately measuring the light transmission of a solution, at 420  $m\mu$  is required.

**Ashing Equipment.**—A silica, or preferably a platinum, dish and a muffle furnace at 900°C.

**Other Apparatus.**—One 250- and six 100-ml. volumetric flasks; 25- and 100-ml. graduated cylinders; 250-ml. beaker; hot plate.

**Reagents.** Hydrochloric Acid.—Concentrated HCl.

Ammonium Sulfate,  $(\text{NH}_4)_2\text{SO}_4$ .

Sulfuric Acid.—Concentrated  $\text{H}_2\text{SO}_4$  and 1:1  $\text{H}_2\text{SO}_4$ .

**Standard Titanium Dioxide.**—Obtainable from the National Bureau of Standards with analysis.

**Hydrogen Peroxide, 3%  $\text{H}_2\text{O}_2$ .**—Dilute 10 ml. of reagent grade 30%  $\text{H}_2\text{O}_2$  to 100 ml. with distilled water. This solution is sufficiently stable for 5 days.

**Calibration.**—Calibrate the photometric apparatus as follows: dissolve the equivalent of 0.10 g. of  $\text{TiO}_2$  in the standard sample, in 10 g. of  $(\text{NH}_4)_2\text{SO}_4$  and 35 ml. of concentrated  $\text{H}_2\text{SO}_4$ . Add 90 ml. of water, filter through a fine paper into a 200-ml. volumetric flask and wash. Cool, dilute to volume, and mix. One milliliter of this solution contains 0.0005 g. of  $\text{TiO}_2$ . Transfer aliquots of 5, 10, 15, 20, 25, and 30 ml. respectively, to 100-ml. volumetric flasks and add 20 ml. of 1:1  $\text{H}_2\text{SO}_4$  to each portion. Add 15 ml. of 3%  $\text{H}_2\text{O}_2$  to each, dilute to volume, mix, and measure their transmittance at 420  $m\mu$ , preferably in a  $\frac{1}{2}$  cm. cell. Plot the transmittance versus the concentration of  $\text{TiO}_2$  on semilog paper, using the linear scale for the concentration of  $\text{TiO}_2$ . Draw a curve through the plotted points.

an inlet tube added to a 3-hole stopper for the 500-ml. flask. This obviates the intensive reaction that occurs when the  $\text{Na}_2\text{CO}_3$  solution is sucked back into the flask. If a  $\text{CO}_2$  cylinder is employed, attach it to an inlet tube provided in the stopper of the flask and flush out the connecting tubing to remove the air and allow a very slow stream of  $\text{CO}_2$  to continue to pass during the reduction. After the reduction and when the solution in the flask has been boiled 3 to 5 minutes, pass  $\text{CO}_2$  into the flask before removing the heat to prevent the liquid in the beaker from being sucked back. If the  $\text{CO}_2$  cylinder is used, water may be substituted for the  $\text{NaHCO}_3$  solution in the beaker.

<sup>97</sup> Because of the rapid oxidation of titanium as soon as the stopper is removed, it may be preferred to add a small (35 ml.) separating funnel to the rubber stopper, and when the solution is cooled, add, through the funnel, an excess of ferric ammonium sulfate; remove the stopper; and titrate the reduced iron with standardized potassium dichromate.

In the absence of knowledge regarding the respective nonfibrous materials present, qualitative tests for sizing (rosin, starch, glue, casein), saturants (waxes, organic saturants, etc.), mineral fillers (especially  $\text{CaSO}_3$  and  $\text{ZnS}$ ), and any other suspected nonfibrous materials should be made before weighing out specimens for test.

**Procedure.**—Allow the specimen to come to moisture equilibrium with the atmosphere of the balance. Weight about 1.5 g. (to the nearest 10 mg.) of the ground paper. Weigh at the same time samples for moisture and ash determinations, and for determination of such other sizing, filling, or other nonfibrous materials as may be found necessary for correction of the copper number. These determinations shall be made by the TAPPI standard methods.

Immediately before use add 5.0 ml. of copper sulfate solution to 95 ml. of carbonate-bicarbonate solution. Bring the mixture to a boil in 2 minutes, and pour it over 1.5 g. of the ground sample in a 125-ml. Erlenmeyer flask. Stir well with a glass rod in order to distribute the fibers and to remove air bubbles. Fit the flask with a loosely fitting glass bulb or stopper and submerge completely in a steam bath at atmospheric pressure. Occasionally fibers tend to float to the surface, therefore the flask should be shaken from time to time to redistribute them. Remove the flask from the steam bath at the end of 3 hours. Filter on an ashless filter paper in a 7.5-cm. Büchner funnel, using suction. Wash by flooding with 100 ml. of 5%  $\text{Na}_2\text{CO}_3$  solution at about  $20^\circ\text{C}$ . and then by flooding with 250 ml. of hot water (about  $95^\circ\text{C}$ .), discarding the filtrates. Transfer the fibers and filter paper to a small beaker, add 25 ml. of the molybdophosphoric acid solution and macerate well with a flattened glass rod. Transfer to a Büchner funnel again and wash thoroughly with cold water until the blue molybdenum color is removed from the fibers. Dilute the filtrate with water to approximately 700 ml. and titrate it with 0.05  $N$   $\text{KMnO}_4$  to a faint pink.

**NOTE.**—The amount of copper sulfate solution given above is sufficient for a copper number not greater than approximately 6, and this figure is seldom exceeded except in papers containing highly lignified fibers, such as groundwood, or in papers which have deteriorated considerably. If the copper number exceeds 6, increase the amount of copper sulfate solution to 10 ml. and the amount of molybdophosphoric solution to 50 ml., or as much more as may be necessary, retaining the correct ratio between the solutions.

**Calculation.**—The copper number is defined as the number of grams of metallic Cu in the  $\text{Cu}_2\text{O}$  resulting from the reduction of the  $\text{CuSO}_4$  by 100 g. of the paper fibers. This is calculated by the formula:

$$\text{Copper number} = \frac{6.36 \times \text{ml. KMnO}_4 \times N}{W},$$

where  $N$  is the normality of the  $\text{KMnO}_4$ , and  $W$  is the weight in grams of the test specimen after deduction of the weight of the nonfibrous materials. Correction of the weight of the test specimen shall always be made for moisture and ash. Correction for other nonfibrous components shall be made whenever they are present in significant amounts. Not less than two determinations shall be made and the average of the results, rounded off to the nearest 0.1, shall be reported. Duplicate determinations should agree within 0.2.

**Report.**—The copper number shall be reported to one decimal place on the basis of total fiber content.

**Additional Information.**—This method is essentially the Braidy<sup>99</sup> modification

<sup>99</sup> Clibbens, D., and Geake, A., J. Textile Inst., 15, T31, 1924.

of the original Schwalbe<sup>100</sup> method, with modifications for its adaptation to paper proposed by Scribner and Brode<sup>101</sup> and by Burton and Rasch<sup>102</sup>

Wilson, Harvey and Padgett<sup>103</sup> have found that melamine formaldehyde resin in paper produces a decrease (0.2 to 0.4) in the copper number of the paper

### ACID-SOLUBLE IRON IN PAPER<sup>104</sup>

The procedure commonly used for this purpose is to extract the ash of the paper with acid, but investigation has shown that the procedure described below is preferable because (1) it requires less time (2) in the ashing of the paper, some of the soluble iron may be volatilized and some of the insoluble iron may be made soluble. The removal of the acid soluble iron is complete. This is considered the portion of the iron present that is potentially chemically reactive as distinguished from insoluble or 'fixed' iron such as might occur as silicate or other complex compound in clay filler. This method is standardized as TAPPI T 434 m 47.

**Reagents** Ammonium Thiocyanate Solution—Dissolve approximately 76 g of pure  $\text{NH}_4\text{SCN}$  in water and dilute to 1 liter.

**Standard Iron Solution**—Dissolve 14.04 g of pure ferrous ammonium sulfate  $\text{Fe}(\text{NH}_4)_2(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$  and 4.07 g of pure ammonium persulfate  $(\text{NH}_4)_2\text{S}_2\text{O}_8$  in water containing 1 ml of concentrated  $\text{H}_2\text{SO}_4$ . Mix well and dilute to exactly 1 liter. Dilute 25 ml of this solution to about 500 ml, add 20 ml of concentrated  $\text{H}_2\text{SO}_4$ , transfer to a 1 liter volumetric flask and dilute to the mark. For 1 g of paper 1 ml of this standard equals 50 parts of Fe per million parts of paper.

**Test Specimen**—The specimen for test shall be cut from the sample in such a way as to be thoroughly representative of it and shall be either cut in small squares (about  $\frac{1}{4}$  in.) or ground. Cutting the paper in small pieces is generally sufficient, but grinding of very hard resistant paper may be found necessary.

**Procedure**—Drench 5 g of paper with 50 ml of concentrated  $\text{HCl}$ . Cold acid usually suffices, but hot acid may be required if large particles of iron are present. After the paper is thoroughly saturated with the acid, filter on a 7.5 cm Buchner funnel. Wash the residue with three 50 ml. portions of hot water, applying suction after each addition. Add a few drops of concentrated  $\text{HNO}_3$  to the combined filtrates, make ammoniacal with concentrated  $\text{NH}_4\text{OH}$ , and boil until the odor of  $\text{NH}_3$  is nearly but not quite gone. Filter through a filter paper and wash the residue on the paper thoroughly with hot water. Place the funnel containing the filter paper and  $\text{Fe}(\text{OH})_3$  in the neck of a 50 ml volumetric flask, and add two successive 5 ml portions of diluted  $\text{HCl}$  (1:3), with intermediate and final washing with water. Dilute the filtrate to 50 ml. Measure 10 ml of this solution equivalent to 1 g of the paper, into a 50 ml Nessler tube and add enough 0.05 N (or 0.1 N)  $\text{KMnO}_4$  solution to completely oxidize the iron, or until there is a faint pink color to the solution. Add 10 ml of the  $\text{NH}_4\text{SCN}$  solution, dilute to the mark, mix, and compare immediately with standards made in the same way with the standard iron solution.

The standard iron comparates shall be prepared freshly for each comparison, as

<sup>100</sup> Schwalbe, C., *Die Chemie der Cellulose*, p. 625, 1912.

<sup>101</sup> Scribner, B. W., and Brode, W. R., *Natl. Bur. Standards Technologic Paper No. 341*

<sup>102</sup> Burton, J. O., and Rasch, R. H., *J. Research Natl. Bur. Standards*, 6, 603 April, 1931  
RP295. Includes description of Koerner type grinder.

<sup>103</sup> Wilson, W. K., Harvey, J. L., and Padgett, A. A., *Tappi*, 34, 410, Sept. 1951

<sup>104</sup> American Public Health Association, *Standard Methods of Water Analysis* 1935

they fade rapidly. A blank determination on the reagents shall be run and a correction applied if necessary. At least two determinations shall be made, and the average of the results shall be reported. Duplicate determinations should agree within 5 parts per million.

Report.—The average result shall be reported as parts of acid-soluble iron per million parts of paper by weight.

### HYDROGEN ION CONCENTRATION (pH) OF PAPER EXTRACTS

In this method the pH value of a paper refers to its acidity or alkalinity in terms of hydrogen ion concentration of the unfiltered aqueous extract of the cut or ground paper.

Both hot- and cold-extraction procedures are included. The hot extraction is customarily used in the paper industry for predicting the stability of papers. The cold-extraction method also is suitable for this purpose and possesses the advantage of being simpler and requiring less working time. It is believed that the cold-extraction method more nearly approaches the normal pH of the paper at the time of the determination. Launer<sup>105</sup> has shown that in the acid region the pH values for cold extraction are higher than those of hot extraction because of the hydrolysis of aluminum sulfate at the higher temperature. Discussions of such points as cold *vs.* hot extraction, purity of the water, time of extraction, etc., can be found in the literature.<sup>106, 107, 108, 109, 110</sup> This method is standardized as ASTM D778-50 and TAPPI T 435 m-52.

**Apparatus.**—The special apparatus required for this test is a circuit including a glass electrode and a saturated KCl-calomel half-cell capable of precision to within 0.1 pH. The complete apparatus is commercially available. The apparatus used shall be standardized frequently against 0.05 *M* potassium acid phthalate solution which has a pH of 4.0 over the entire range of room temperature.

If a disintegrator is used, the Koerner type or its equivalent is recommended. Alternatively, a sharp rasp or grater may be used. Care is necessary to neither contaminate nor unduly heat the paper during disintegration.

**Reagents.** Potassium Acid Phthalate Solution, 0.05 *M*.—For standardizing the electrode. Dissolve 10.2 g. of  $\text{KHC}_8\text{H}_4\text{O}_4$ , sufficiently pure for acidimetric purposes, in water and dilute to 1 liter. This solution generally will remain usable for several months at pH 4.0.

**Distilled Water.**—For making the extraction, water containing ordinary amounts of  $\text{CO}_2$ , but not more than corresponds to a pH of 5.9, may be used to test all papers, including those in the neutral range between pH 6.0 and 7.0. A sample of the water must be tested for alkaline impurities, however, by boiling for a few minutes, cooling, and then measuring its pH. If this is found to be higher than

<sup>105</sup> Launer, H. F., J. Research Natl. Bur. Standards, 22, 553, 1939; Research Paper RP1205.

<sup>106</sup> Wehmhoff, B. L., Tech. Assoc. Papers, 13, 231, May, 1930; *Ibid.*, 14, 387, May, 1931.

<sup>107</sup> Burton, J. O., and Rasch, R. H., J. Research Natl. Bur. Standards, 6, 603, 1931. This contains a description of the Koerner disintegrator.

<sup>108</sup> Browning, B. L., and Ulm, R. W. K., Paper Trade J., 102, 89, Feb. 20, 1936.

<sup>109</sup> Launer, H. F., J. Research Natl. Bur. Standards, 23, 663, 1939; Research Paper RP1262.

<sup>110</sup> Wehmer, P. F., Tech. Assoc. Papers, 23, 56, 446, 1940.

73 the water must be distilled from a solution containing approximately 1 g of  $\text{KMnO}_4$  and 4 g of  $\text{NaOH}$  per liter. A double still head is usually necessary.

**Test Specimens**—The test specimen shall be cut from the sample in such a way as to be thoroughly representative of it. Ordinary papers such as printing and writing papers may be tested in the form of cuttings roughly 1 sq cm in area. If however the paper is more than 0.012 in thick or extremely dense it shall be reduced to a fluffy form by a disintegrator. The prepared material shall be thoroughly mixed.

**NOTE** The use of a disintegrator should be avoided except when necessary because of possible contamination. When using a Koerner type disintegrator if the size of the sample will permit it is well to run a considerable amount of the paper through the disintegrator and discard it before preparing the sample for test.

**Procedure Cold Extraction**—Weigh 10 g of the air dry cut or ground paper into a 100 ml beaker. Add about 20 ml of distilled water and macerate with a flattened stirring rod until the specimen is uniformly wet. Then add 50 ml more of the water stir well cover with a watch glass and let stand for 1 hour. At the end of the extraction period stir once more and measure the pH of the unfiltered mixture with the glass electrode. Carry out the entire procedure at 20 to 30°C (68 to 86°F). If the glass electrode had just previously been used for measurements in the alkaline region and if the paper to be tested is in the neutral region immerse the electrode in 0.05 M potassium acid phthalate for 1 minute and rinse thoroughly several times with distilled water before use.

**Hot Extraction**—Weigh 10 g of the air dry cut or ground paper into a 125-ml Erlenmeyer flask. Add about 20 ml of distilled water and macerate with a flattened stirring rod until the specimen is uniformly wet. Then add 50 ml more of the water stir and affix to the flask a stopper containing a glass tube about 9 mm in diameter and 75 cm in length which serves as a condenser. A soil digestion flask which has a ground glass stopper and condensing tube in one piece or a rubber stopper covered with clean metal foil may be used. Place the flask in a steam bath which will maintain the contents of the flask at 95 to 100°C and boil out the water. Heat at this temperature for 1 hour with occasional shaking then cool to 20 to 30°C (68 to 86°F) and measure the pH of the unfiltered mixture with the glass electrode. If the glass electrode had just previously been used for measurements in the alkaline region and if the paper to be tested is in the neutral region immerse the electrode in 0.05 M potassium acid phthalate for 1 minute and rinse thoroughly several times with distilled water before use.

**Report**—All tests shall be made in duplicate the results of which should agree within 0.1 pH. The average shall be expressed to the nearest 0.1 pH. The report shall state whether cold extraction or hot extraction was used.

**Additional Information**—In Table 38.7 pH values are expressed in terms of hydrogen and hydroxyl ion concentrations. This table emphasizes the importance of small differences in pH at the extreme ends of the acid and alkali range usual to papers as contrasted with the relative unimportance of numerically equal differences in pH in the neutral region.

Wilson, Harvey and Padgett<sup>111</sup> have found that during hot water extraction melamine formaldehyde resin hydrolyzes releasing alkaline products. As a result the hot extraction pH of a paper containing both alum and melamine resin may

<sup>111</sup> Wilson, W. K., Harvey, J. L. and Padgett, A. A. Tappi 34: 410-15 Sept. 1951.

TABLE 38-7. CORRESPONDING pH, H-ION AND OH-ION VALUES

<i>pH</i>	<i>H-ion</i> <i>concentration</i>	<i>pH</i>	<i>OH-ion</i> <i>concentration</i>
4.0	1000 $\times 10^{-7}$	7.0	1 $\times 10^{-7}$
4.1	790	7.1	1.3
4.2	630	7.2	1.6
4.3	500	7.3	2
4.4	400	7.4	2.5
4.5	320	7.5	3
4.6	250	7.6	4
4.7	200	7.7	5
4.8	160	7.8	6
4.9	130	7.9	8
5.0	100	8.0	10
5.1	79	8.1	13
5.2	63	8.2	16
5.3	50	8.3	20
5.4	40	8.4	25
5.5	32	8.5	32
5.6	25	8.6	40
5.7	20	8.7	50
5.8	16	8.8	63
5.9	13	8.9	79
6.0	10	9.0	100
6.1	8	9.1	130
6.2	6	9.2	160
6.3	5	9.3	200
6.4	4	9.4	250
6.5	3	9.5	320
6.6	2.5	9.6	400
6.7	2	9.7	500
6.8	1.6	9.8	630
6.9	1.3	9.9	790
7.0	1	10.0	1000

be higher, lower, or equal to the cold-water pH, depending on the relative amounts of alum and resin present.

#### ALKALI-STAINING RESISTANCE OF PAPER <sup>112</sup>

It is desirable that certain papers, particularly those used as soap wrappers, should not stain unduly with alkali. In the past this property has been generally judged by dropping upon the paper alkaline solutions of varying strengths. The present method is designed for a quantitative statement of the resistance to alkali staining. This method is standardized as ASTM D723-45 and TAPPI T 440 m-53.

<sup>112</sup> Crossley, T. Lindsey, A Quantitative Test for Soap Wrap Paper, Tech. Assoc. Papers, 20, 208, 1937.



This method is applicable to undyed papers. It is not advised for use with pulps. It can be used with hard sized (rosin) papers by first removing the major part of the sizing with ether or methanol.

**Apparatus** Nessler Tubes—A set of six is convenient. They should be made with thin colorless walls 1 mm thick, have a diameter of 29 to 30 mm and the 50 ml mark should be about 90 mm from the bottom outside.

**Precision Pipet**—Capacity 1 ml graduated to 0.01 ml.

**Reagents** Potassium Bichromate Solution—Dissolve 0.25 g of  $K_2CrO_4$  in a small amount of water and dilute to 1 liter.

**Congo Red Solution**—Make up a 0.05% solution in water. Eastman Kodak Company Congo Red E.K. 770 is recommended.

**Normal Sodium Hydroxide Solution**

**Test Specimen** The test specimen shall consist of 3.00 g of the paper torn into pieces  $\frac{1}{4}$  to  $\frac{1}{2}$  in square. With vegetable parchment a finer subdivision of the sample is advisable.

**Procedure**—Place the test specimen in a 250 ml Erlenmeyer flask, add 50 ml of hot water and boil for 5 minutes. Decant off the liquid into a 100 ml volumetric flask or graduated cylinder. Add 50 ml of hot water to the paper in the flask and boil again for 5 minutes. Decant the second liquid into the first and make up to 100 ml using the make up water to wash the paper in the flask.

Add 25 ml of normal NaOH solution to the combined liquids and after letting stand for at least 5 minutes filter using a fast filter paper if the insoluble matter is flocculent or a close filter if it appears cloudy. Compare the clear filtrate with standards made as follows:

To 50 ml of the bichromate solution add 0.1 ml of the Congo red solution and mix well. Exact matches of tint are not always possible but distinction in intensity is readily seen. Place different amounts of this mixed solution such as 0.2, 0.5, 1.0, 2.0 ml each in separate Nessler tubes dilute to the 50 ml mark with water and mix.

Place 50 ml of the filtered alkaline solution from the paper in another Nessler tube and compare with the standards.

The solutions are best compared by holding the tubes containing them over white paper but not resting on it and looking down through the solutions. If none of the standards matches the solution make up standards of other strengths and compare them with the solution. As bichromate slowly destroys the Congo red color the solution should not be mixed until immediately before use.

**Report**—Report the number of milliliters of bichromate Congo red solution required to match the tint of the alkaline extract of paper as the *alkali staining number*. Express the results to 1 decimal place.

**Interpretation of Results**—It has been found that papers showing an alkali staining number of more than 3 will give a marked stain with 1% sodium hydroxide solution by the drop test.

## PENTOSANS IN PAPER<sup>113</sup>

In this method the furfural formed by the action of hot hydrochloric acid on the fibrous material is distilled from the mixture in essentially the manner prescribed by the AOAC.<sup>114</sup> The distillates are analyzed for furfural by a rapid

<sup>113</sup> Weimer P. F. Tech. Assoc. Papers 23, 446-48 June 1940.

<sup>114</sup> Assoc. Official Agricultural Chemists. Methods of Analysis 4th ed. p. 344 1935.

volumetric procedure requiring no complicated apparatus. The volatile material, probably hydroxymethylfurfural, arising from the action of HCl upon the cellulose in the samples is corrected for in a simple manner. The correction was found to be valid for the typical chemical wood fibers and papers made therefrom, including unbleached sulfate. This correction is described by Launer and Wilson,<sup>115</sup> who also show that the pentosan values for cotton fiber are negligible, being probably less than 0.2%. This method is standardized as ASTM D688-44 and TAPPI T 450 m-44.

**Apparatus.**—The special apparatus required for this test is a disintegrator which will completely disintegrate the sample without heating or contaminating it. A Koerner type<sup>116</sup> or its equivalent shall be used.

For the distillation a 300-ml. separatory or dropping funnel is mounted in the neck of a 500-ml. distilling flask, which in turn is connected to a long water-cooled condenser. The condenser delivers through an adapter into a 1-liter glass-stoppered reagent bottle which is used as a receiver and subsequently as a reaction vessel. Rubber stoppers may be used to make the connections. If the temperature of the condensate in the receiver is 30°C. (86°F.) or over, owing to inefficient cooling or high laboratory temperature, a small U trap, containing glass beads and 5 ml. of water, should be used to close off the system.

**Reagents.** Hydrochloric Acid, 3.5 N (12%).—Dilute 307 ml. of c.p. concentrated HCl (sp. gr. 1.18–1.19) to 1 liter.

**Ice.**—Preferably frozen from distilled water. Ordinary commercial ice is satisfactory if uniform values for the blank determinations (see below) are obtained with it.

**Potassium Iodide Solution, 10%.**—Dissolve 10 g. of c.p. KI in 90 ml. of water.

**Sodium Thiosulfate Solution, 0.1 N.**—Dissolve 25.3 g. of c.p.  $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$  in water containing 1 ml. of 1 N NaOH and dilute to 1 liter. This gives a solution slightly stronger than 0.1 N, but subsequent calculations are thus made easier. After one week, standardize the solution against 0.1 N permanganate as follows:

Add 120 ml. of approximately 6 N  $\text{H}_2\text{SO}_4$  to 320 ml. of water in a 1-liter glass-stoppered reagent bottle. Follow with 10 ml. of 10% KI solution and then, after shaking, add 50 ml. of 0.1 N  $\text{KMnO}_4$  solution from a pipet. After shaking again, titrate with the thiosulfate solution, adding starch indicator toward the end of the titration.

**Potassium Bromate-Bromide Solution, 0.2 N.**—Dissolve 5.57 g. of c.p.  $\text{KBrO}_3$  and 50 g. of c.p. KBr in water. Add 1 ml. of N NaOH and dilute to 1 liter. The solution is not standardized, but blank determinations against the thiosulfate solution are made at intervals, as described below.

**Test Specimen.**—The test specimen shall be representative of the sample, and shall be reduced to an open fluffy form in the disintegrator and then thoroughly mixed.

**Procedure.**—Allow the sample to come to moisture equilibrium with the atmosphere of the balance. Weigh, to the nearest milligram, duplicate 1-g. samples of the ground, air-dry material for the pentosan determination. Weigh at the same time specimens for the determination of moisture, ash, and sizing materials. Introduce the test specimen into the distilling flask through a clean, dry glass tube so

<sup>115</sup> Launer, H. F., and Wilson, W. K., J. Research Natl. Bur. Standards, 22, 471, 1939; Research Paper RP1199.

<sup>116</sup> Burton, J. O., and Rasch, R. H., J. Research Natl. Bur. Standards, 6, 603, 1931; Research Paper RP295.

as to avoid adherence of fibers to the neck of the flask. Add 100 ml of 3.0 N HCl to the flask marking the flask to indicate this volume. Then fit the dropping funnel containing 300 ml of 3.0 N HCl in the neck of the flask and apply heat from a burner. As soon as distillation begins let the acid drip from the funnel at such a rate that the level in the flask remains constant. Continue the distillation at a uniform rate for 100 minutes during which period 300 ml of condensate should have been collected. It is important to observe time and quantity. The rate of distillation can be observed by marking the receiver at 100, 200 and 300 ml.

Add 50 ml of water to the condensate (if a trap was used as described above combine its contents with the condensate and add correspondingly less water) and then add 250 g of crushed ice. After the temperature of the mixture has fallen to 0°C or lower add 20 ml of 0.2 N bromate bromide solution from a pipet with minimum agitation close the bottle promptly with a ground glass stopper shake well and let stand for exactly 5 minutes. The temperature should still be 0°C or lower. Then remove the stopper add 10 ml of 10% KI from a small graduate and replace the stopper as quickly as possible. Shake the mixture thoroughly to allow absorption of the Br vapor and titrate with 0.1 N thiosulfate solution until colorless using starch indicator toward the end of the titration.

Determine the blank in exactly the same manner using all reagents including the ice except that the starting point is 270 ml of 3.0 N HCl diluted to 350 ml instead of 300 ml of condensate plus 50 ml of water.

Calculation of Results.—The pentosan content of the paper is calculated by substitution in the following formula

$$\text{Pentosans, \%} = \frac{7.5 \text{ N } (v_2 - v_1)}{W} - 1.0,$$

where  $N$  = normality of thiosulfate solution,

$v_1$  = volume of thiosulfate solution used in test,

$v_2$  = volume of thiosulfate solution used in blank,

and  $W$  = weight of specimen after correcting for moisture, ash, and any filling and sizing materials present.

NOTE.—The factor 7.5 is the product of

$$\frac{100 \times 0.048}{0.727 \times 0.88}$$

where 0.048 is the weight of furfural in grams corresponding to 1 ml of 1 N thiosulfate solution. 0.727 is the theoretical conversion factor of pentosans to furfural and 0.88 is a factor to compensate for the incomplete conversion of pentosans to furfural. The correction factor of 1.0 is applied to compensate for the hydroxymethylfurfural arising from the cellulose.

The factor 0.88 is based upon the observation that the yield of furfural from xylan is 88% of the theoretical in this method of distillation. The corresponding value for arabinose is 74% and a furfural yield of 80% is frequently taken as an approximate average in calculating furfural yields to pentosans. However, since xylan constitutes most if not all of the pentosans in wood pulp it appears preferable to use the factor 0.88. If both araban and xylan are present the above equation becomes

$$\text{Pentosans, \%} = \frac{8.25 \text{ N } (v_2 - v_1)}{W} - 1.1$$

This equation with the omission of the 1.1% correction, gives values which are comparable with those obtained by using Kroker's tables in which the conversion of pentosans to furfural is also arbitrarily taken as 80%.

The factors 0.80 and 0.88 which are applied to compensate for the incomplete conversion of pentosans to furfural are somewhat arbitrary. If the analyst desires values in which these factors do not appear, and in which the furfural actually obtained is converted to equivalent pentosans, a *minimum pentosan content* may be calculated by the equation

$$\text{Pentosans, \%} = \frac{6.80 N (v_2 - v_1)}{W} - 0.9,$$

where the factor 6.80 is the product of  $\frac{1.03 \times 0.0480 \times 100}{0.727}$ . The factor 1.03 is the correction necessary to account for the destruction of furfural during the distillation. The constant 0.9 corrects for hydroxymethylfurfural.

**Report.**—The pentosans shall be reported as a percentage of the total cellulose, including pentosans but excluding moisture, ash (fillers), resin, or any other added nonfibrous materials. All determinations of pentosans shall be made in duplicate, the results of which shall agree within 0.4 or less, and the average shall be expressed to the nearest 0.1.

### TURPENTINE TEST FOR GREASE RESISTANCE OF PAPER

This method gives an accelerated comparison of the relative rates at which ordinary oils or greases, such as commonly found in foodstuffs, may be expected to penetrate papers such as uncoated or unimpregnated greaseproof, glassine, and vegetable parchment. This method is standardized as ASTM D722-45 and TAPPI T 454 m 60

**Apparatus. Tube.**—Of any rigid material, 1 in. inside diameter and not less than 1 in. in height, the ends of which have been smoothed.

**Pipet or Medicine Dropper.**—Calibrated to deliver 1.1 ml.

**Round-Grained Sand.**—Ottawa cement testing sand screened to pass a No. 20 and be retained on a No. 30 sieve

**Paper.**—Sheets of white coated and calendered book paper,  $110 \pm 10$  g.s.m. (70 lb 25 x 38–500), at least the same size as the test specimen, conveniently much larger.

**Reagent. Turpentine.**—Colored, water free turpentine, prepared as follows. To 100 ml of pure gum spirits turpentine, c.p. grade, sp. gr. 0.860 to 0.875 at 60°F., add 5 g. of anhydrous calcium chloride and 1.0 g. of oil soluble red dye. Stopper the container, shake well, and let stand for at least 10 hours, shaking occasionally. Then filter through a dry filter paper at a temperature of approximately 70°F., and store in an airtight bottle.

**Test Specimen.**—Prepare at least ten 4 in. square specimens from representative samples taken in accordance with TAPPI Standard T 400 m.

**Procedure.**—The test specimens shall be conditioned in an atmosphere in accordance with TAPPI Standard T 402 m (p. 1795).

Make an equal number of tests on each side of the sample. If possible, note those made on the felt side and on the wire side separately.

Place each specimen on a sheet of the book paper, which rests on a smooth plane surface. Place the end of the tube on the specimen and put 5 g. of sand in the tube. Since the purpose of the tube is solely to assure a uniform area of the sand pile, remove it immediately after the addition of the sand. Using the pipet or medicine dropper, add 1.1 ml. of the colored turpentine to the sand, and note the time.

Move the test specimens to unsoiled positions on the coated paper and examine

the uncovered area of it for staining every 30 seconds for the first 2 minutes every minute for the next 8 minutes and every 3 minutes thereafter. As soon as the first red stain appears on the coated paper note the time. The time elapsed in seconds between the application of the turpentine and the appearance of the first definitely red stain shall be recorded as the transudation period. If any test period extends over 3 hours record it merely as 1800+

**NOTE**—In the absence of knowledge of the probable time of transudation it is advisable to make a few preliminary tests.

**Report** Report the average and maximum and minimum test results in seconds to three significant figures and if possible for both wire side up and felt side up. When a test exceeding 1800 seconds is included in an average report the calculated average followed by a plus sign. The following is an example of the recommended form

<i>Turpentine Test</i> Seconds	<i>Felt</i> Side Up	<i>Wire</i> Side Up
Maximum	1800+	1750
Minimum	1500	1400
Average of 15 tests	1750+	1600
Grand Average	1670+ sec	

### KAPPA NUMBER OF PULP

This method is adapted to the determination of the relative hardness, bleachability or degree of delignification of pulp. For example it may be used for all types and grades of chemical and semichemical unbleached and semibleached wood pulps obtained with a yield of under 70%. For this purpose it is preferred to TAPPI Standard T 214 m p 1769 which is retained mainly for historical reasons. This method is designated T 236 m 60.

The kappa number is the number of milliliters of tenth normal potassium permanganate solution consumed per gram of moisture free pulp under conditions specified in this standard. The results are corrected to be equivalent to a 50% consumption of the permanganate in contact with the specimen.

**Apparatus** **Stirrer**—A propeller type agitator made of glass or other noncorrosive material or a plastic or glass covered magnetic stirrer suitable for a 2000 ml beaker.

**Disintegrator**—For example an electric high speed propeller mixer to separate the pulp sample into individual fibers.

**Reaction Beaker**—2000 ml glass or porcelain.

**Pipets**—Two 100 ml automatic pipets are especially convenient when a large number of determinations are to be made.

**Buret, 50 ml, Graduated to 0.1 ml**—A 52 ml buret, obtainable from some supply houses will be found more convenient for titrating the reaction mixture in the blank test.

**Constant Temperature Bath at  $25 \pm 0.1^\circ\text{C}$** —To contain the 2 liter beaker while stirring.

**Other Apparatus**—A Buchner funnel and filter flask to dewater 3 to 4 g of pulp, stopwatch or clock, a 1 liter, and a 25 or 50 ml graduated cylinder, 250 ml beaker.

**Reagents.** Potassium Permanganate— $0.1 \pm 0.0005$  N  $\text{KMnO}_4$ .—A stock solution of normal  $\text{KMnO}_4$  may be prepared by dissolving 325 g. of dry  $\text{KMnO}_4$  in sufficient distilled water to make 10 liters. Let this solution stand at least 1 month. Pass the solution through a fritted glass filter covered with a carefully made asbestos mat. Store in a dark place. Dilute 1 liter of the stock solution to 10 liters with distilled water, and adjust so that it will be  $0.1 \pm 0.0005$  N when standardized against previously standardized sodium thiosulfate or sodium oxalate.

Sodium Thiosulfate  $0.2$  N  $\text{Na}_2\text{S}_2\text{O}_3$ .—This should be of exact or known strength accurate to  $\pm 0.0005$  N.

Potassium Iodide,  $1.0$  N  $\text{KI}$  (166 g. per Liter).—Reagent grade.

Sulfuric Acid, Approximately  $4$  N  $\text{H}_2\text{SO}_4$ .—Add 112 ml. of reagent grade, concentrated  $\text{H}_2\text{SO}_4$  (94.5 to 96.5%), to about 500 ml. of cold water and dilute to 1 liter. The solution need not be standardized.

Starch Indicator or Thyodine.—The latter gives a sharper end point and is not subject to spoilage.

**Test Sample.**—Obtain a sufficiently large sample to represent the pulp to be tested and prepare a smaller representative sample as follows:

(1) Air-Dried Pulp Sheets.—Tear small pieces from the sample sheets to weigh a total of 3 to 4 g.; do not use a Wiley mill or a similar dry grinding apparatus.

(2) Slush Screened Pulps.—Mix and make 3 to 4 g. (dry weight) into a pad by filtering on the Büchner funnel. Air-dry the pad and tear it into small pieces. Do not use any organic solvent to hasten the drying.

(3) Unscreened Pulps.—If the pulp sample is from unscreened pulp, which is normally screened before bleaching or other processing, remove the shives and knots from the sample by screening, using a method chosen to give results similar to those obtained industrially. Proceed as in (2) above.

Prior to weighing the test specimens, condition the small samples for not less than 20 minutes in the atmosphere near the balance. By trial or experience, weigh to the nearest milligram that amount of pulp that, it is estimated, will consume approximately 50% of the  $\text{KMnO}_4$  used in the test. (The permanganate-consumption by the specimen must be between 30 to 70% to comply with this standard.) At the same time, weigh out a second specimen and determine its moisture content in accordance with ASTM D644-55, p. 1804.

**Procedure.**—Disintegrate the test specimen in 500 ml. or less of distilled water until free from fiber clots and undispersed fiber bundles. Avoid extensive cutting of the fibers but make certain that all the fibers are separated. Transfer the disintegrated specimen to the 2-liter reaction beaker and rinse out the apparatus with enough distilled water to bring the total volume to 795 ml. Adjust the temperature to  $25^\circ\text{C}$ . Place the beaker and contents in the constant-temperature bath and ensure that the temperature stays at  $25^\circ \pm 0.1^\circ\text{C}$ . during the entire reaction. Continuously stir the suspension so as to produce a vortex about 2.5 cm. (1 in.) deep, but not fast enough to introduce air into the mixture.

Pipet 100 ml. of  $0.1$  N  $\text{KMnO}_4$  and 100 ml. of  $4$  N  $\text{H}_2\text{SO}_4$  into a 250-ml. beaker and bring this mixture to  $25^\circ\text{C}$ . Add it quickly to the disintegrated specimen and simultaneously start the stopwatch. Rinse out the 250-ml. beaker, using about 5 ml. of distilled water, and add to the reaction mixture. Its final volume should be  $1000 \pm 5$  ml. At the end of exactly 10.0 minutes, stop the reaction by adding 20 ml. of the  $1.0$  N  $\text{KI}$  from a graduated cylinder.

Immediately after mixing, but without filtering out the fibers, titrate the free

iodine in the suspension with 0.2 N  $\text{Na}_2\text{S}_2\text{O}_3$  adding a few drops of the indicator toward the end of the reaction

Make a blank determination using exactly the same procedure, but without the pulp. In this case the mixture may be titrated with the  $\text{Na}_2\text{S}_2\text{O}_3$  immediately

NOTE—Do not use this blank titration to determine the normality of the  $\text{KMnO}_4$

Calculate the Kappa number  $K$  as follows

$$K = \frac{p \times f}{W}, \quad p = \frac{(b - a)N}{0.1}$$

where  $f$  = factor for correction to a 50% permanganate consumption, dependent on the value of  $p$ ,

$W$  = grams of moisture-free pulp in the specimen,

$p$  = milliliters of 0.1 N permanganate actually consumed by the specimen,

$b$  = milliliters of the thiosulfate consumed in the blank determination,

$a$  = milliliters of the thiosulfate consumed in the test, and

$N$  = normality of the thiosulfate

The factors dependent on the value of  $p$ , are given below, all factors are based on the equation:

$$\log K = \log p/W + 0.00093(p - 50)$$

#### FACTORS $f$ TO CORRECT FOR DIFFERENT PERCENTAGES OF PERMANGANATE USED

$p +$	0	1	2	3	4	5	6	7	8	9
30	0.958	0.960	0.962	0.964	0.966	0.968	0.970	0.973	0.975	0.977
40	0.979	0.981	0.983	0.985	0.987	0.989	0.991	0.994	0.996	0.998
50	1.000	1.002	1.004	1.006	1.009	1.011	1.013	1.015	1.017	1.019
60	1.022	1.024	1.026	1.028	1.030	1.033	1.035	1.037	1.039	1.042
70	1.044									

Report—Report the Kappa number as follows under 100 to nearest 0.1 over 100 to the nearest whole number

If the sample has been screened, briefly report the method used

Precision—The 99% probability at a test level of 112 is about  $\pm 2.5$  Kappa number, consequently, duplicates should check within 2.0%

**Additional Information—Modifications for Routine Control Only** *Correction for Reaction Temperature*—If a temperature bath is not available determine the temperature after the reaction has been taking place for 5 minutes and assume this to be the average reaction temperature throughout the test. If this temperature is not higher than 30°C or lower than 20°C, the Kappa number may be corrected approximately as follows

$$K = \frac{pf}{W} [1 + 0.013(25 - t)]$$

where  $t$  = actual reaction temperature in degrees centigrade and the other symbols are as before.

*Use of Smaller Quantities*—For full chemical pulps, use 50 ml of the  $\text{KMnO}_4$ , 50 ml of the  $\text{H}_2\text{SO}_4$ , 400 ml of water and the appropriate amount of pulp following the standard procedure as given in other respects

*Sample Preparation*—The use of air dry pulp is specified in the procedure. For routine control purposes where time is an important factor, it may be found more

convenient to use slush pulp of a definite consistency, or pulp which has been washed with acetone and dried in an oven to be moisture-free. Slush pulp will give a slightly higher, and oven drying a slightly lower, permanganate consumption.

If the first two modifications above are used for routine control purposes, the results will usually be close to those obtained by the standard method. However, none of these modifications may be considered as complying with the standard procedure and the unavoidable use of any modification, should be stated prominently in the report.

**Relationship with Lignin.**—The Kappa number gives essentially a straight line relationship with both Klason lignin and chlorine number for the pulps below 70% total pulp yield.<sup>117</sup> The percentage of Klason lignin approximately equals  $K \times 0.15$ .

**Aging.**—Freshly made pulp has a slightly higher permanganate consumption than pulp that has stood several days or months. The change is rather rapid immediately after the pulp is made, but reaches a relatively stable stage after 2 or 3 days.

**Conversion Factors.**—The results with this method will be markedly increased from those with T 214 m-50. Conversion factors should be obtained for each type of pulp if present values are to be compared with those from the previous method. For this reason and to avoid confusion, it is desirable to use the term "Kappa number" for this procedure instead of the elsewhere used "K number." The approximate conversions from 40 ml. K numbers according to T 214 m-50, to the present Kappa numbers are shown below:

CONVERSION OF 40 ML. K NUMBERS (T 214 M-50) TO KAPPA NUMBERS

40 ml. K. no.	Kappa no.	40 ml. K. no.	Kappa no.
8	12.4	22	35.4
10	14.5	24	41.0
12	16.3	26	47.5
14	19.5	28	55.2
16	22.5	30	64.1
18	26.2	32	73.8
20	30.4	34	85.6

The above conversion factors may be calculated from the formula:  $\log \text{Kappa no.} = 0.837 + 0.0323 (40 \text{ ml. K no.})$ .

**General.**—For years there has been a need for a comprehensive method to determine the permanganate consumption of both high lignin content pulps and well-cooked pulps. A problem with the original permanganate method has been the discontinuity produced by a change in the weight of the specimen or in the amount of permanganate added, since a change in their relative properties causes a substantial change in the permanganate consumed. This difficulty is avoided in the present method by expressing the permanganate consumption at a fixed concentration.

A straight-line relationship exists between the concentration of permanganate at the end of the reaction, and the logarithm of the permanganate consumption. This relationship is substantially independent of the type of pulp or the magnitude of

<sup>117</sup> Tasman, J. E., and Belzins, V., *Tappi*, 40, No. 9, 691-704, Sept. 1957; *Pulp Paper Mag. Canada*, 58, No. 10, 115-58, Sept. 1957.



the permanganate consumption. This enables the permanganate consumption of all pulps to be expressed at a single concentration (50%) by applying a conversion factor and permits the direct comparison of analytical data throughout the entire range of chemical and semichemical pulps. However with increasing lignin content the permanganate consumption levels off and finally decreases as the yield of pulp rises over 70% of the original wood. For this reason no permanganate test is a reliable indication of the degree of pulping of an extremely raw pulp.

This method is practically identical to International Committee for Chemical Analyses Method ICCA 159 which has been adopted by most of the pulp producing countries in the world.

## Chapter 39

# PESTICIDES

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### AEROSOL INSECTICIDES

#### NONVOLATILE INGREDIENTS FROM LOW-PRESSURE TYPE AEROSOLS CONTAINING A MIXTURE OF PROPELLANTS FREON-11 AND FREON-12

*Procedure.*—Weigh the dispenser and contents, cool in a dry ice chamber or other satisfactory cooler, such as a refrigerator freezing compartment, for about 30 min.; punch a very small hole in the top of the container, and allow it to stand in a hood at room temperature while the propellant gas (Freon-12) escapes. After the Freon-12 has volatilized, carefully cut off the top of the container, and heat the residue in a water bath for 40 min. at 88°C. to expel the Freon-11. Cool to room temperature, and weigh the container with the nonvolatile material. Transfer the nonvolatile material to a suitable container, and retain it for analysis. Rinse the aerosol container with ether, dry, and weigh. The difference between these weights represent the weight of nonvolatile material in the aerosol. Weigh the top of the container, which had previously been removed, add this weight to that of the empty and dried container, and subtract their combined weight from the original gross weight of the aerosol to obtain the net content. Calculate and report the percentage of nonvolatile residue obtained from the aerosol.

#### ANALYSIS OF THE COMPONENTS IN THE NONVOLATILE MATERIAL

##### PYRETHRINS

Pyrethrins I and II may be determined in the presence of naphthalene oils, sesame, and piperonyl butoxide (p. 1897). In the presence of sesame oil, however, additional barium chloride is required to precipitate the soaps formed from the saponification of the sesame, and, consequently, the amount of sulfuric acid (1:4) should be increased. Cyclohexanone seriously interferes with the determination of Pyrethrin II, so it is only necessary to determine Pyrethrin I, and multiply its value by 2 to obtain the approximate percentages of total pyrethrins. A 3 to 5 g. sample of the nonvolatile residue is usually sufficient for the determination of the pyrethrins.

## DDT OR METHOXYCHLOR

The total chlorine in either of these ingredients may be determined by an appropriate DDT procedure (p 1860) A small quantity of Freon 11 may remain with the nonvolatile material however and must be removed prior to analysis A satisfactory procedure is as follows transfer a sample containing approximately 0.033 to 0.035 g of chlorine to a 250-ml Erlenmeyer flask add 10 ml of acetone and evaporate on a steam bath add 10 ml more of acetone and again evaporate This treatment will remove all the Freon 11 which boils at 25°C and should not remove any DDT or methoxychlor

## MIXTURES OF DDT AND METHOXYCHLOR

Mixtures of DDT and methoxychlor appear in some aerosols and may be determined by the partition chromatographic method with the following technique

**Procedure** Weigh about 10 ml of the nonvolatile matter into a 50 ml volumetric flask Add 1 ml of mixed dye and dilute to volume with mobile solvent Collect and combine the DDT fractions in the usual manner employing the long column (100 g silicic acid etc) These fractions will contain in addition to the DDT mineral oil and probably other contaminants Determine the total chlorine in these fractions and calculate its percentage to DDT

After the last trace of violet dye is off the column collect and discard about 80 ml of effluent mobile solvent Then begin to take and evaporate 10 ml fractions After the 2,2-bis(*p*-methoxyphenyl)-1,1,1-trichloroethane appears continue to collect 10 ml fractions until all the *p*-methoxychlor has passed through the column (usually 8 to 10 fractions are sufficient) Combine the fractions containing the *p*-methoxychlor remove the solvent and weigh Calculate the percentage of total methoxychlor on the basis that the technical product contains a minimum of 88% of the *p* isomer

## DETECTION OF METHYLATED AROMATIC PETROLEUM DERIVATIVE OILS (METHYL NAPHTHALENE OILS)

Methylated aromatic petroleum derivative solvent oils frequently occur in aerosols

**Procedure**—Add several drops of the nonvolatile residue to 15 ml of a saturated solution of picric acid in a 125 ml Erlenmeyer flask and shake vigorously A formation of an orange yellow to reddish orange precipitate of a picrate naphthalene derivative is indicative of their presence

## DETECTION OF SESAME OIL

**Procedure** Add 2 ml of furfural to 100 ml of alcohol Mix thoroughly 0.1 ml of this solution with 10 ml of hydrochloric acid and 5–10 ml of the sample by shaking them together in a test tube for 15 sec Allow mixture to stand for 10 min observe color add 10 ml of water shake and again observe color If the crimson color disappears sesame oil is not present (As furfural gives a violet tint with hydrochloric acid it is necessary to use the very dilute solution specified)

## DETECTION OF PIPEROYL BUTOXIDE

**Reagent**—Dissolve 0.05 g of tannic acid in 15 ml of glacial acetic acid by shaking at room temperature When the tannic acid is all in solution add 35 ml of

85% phosphoric acid and thoroughly mix the solution. This reagent should be freshly prepared for each day's determinations, and should be kept tightly stoppered because it is hygroscopic.

**Procedure.**—Dilute a sample of the nonvolatile residue with odorless base oil so that it will contain approximately 50 mg. of piperonyl butoxide per 100 ml. of solution. Transfer 0.1 ml. of the diluted solution to an 18 by 150 mm. test tube, and add 5 ml. of the reagent. Shake the tube vigorously for 30 sec., and then put it in a bath of boiling water for 5 min. A blue color will develop in the presence of piperonyl butoxide.

## ALDRIN

### INFRARED METHOD

**Reagents.** Aldrin.—99.9% purity, m.p. 102.7 to 102.8°.

Carbon Disulfide, Spectral Grade.—Check transmittancy at 8.48  $\mu$ .

**Procedure.**—A predetermined volume of carbon disulfide is accurately measured into the vial or flask containing the aldrin. A concentration of aldrin, of 0.05% w/v, falls about in the middle of the calibration curve. The concentration unit is defined as the weight in grams of insecticide per 100 ml. of solution; for example, 0.05% aldrin refers to a solution containing 0.05 g. of aldrin in 100 ml. of solution. If the sample contains 100  $\mu$ g. of aldrin, 0.20 ml. of carbon disulfide is added to obtain a concentration of 0.05%.

The container is thoroughly shaken in order to dissolve the aldrin completely. This solution is then transferred through the tapered fitting of an absorption microcell with a syringe, with the cell held in a vertical position so that the tapered fitting is at the bottom. The cell is filled carefully to be free of air bubbles, and stoppered with a small rubber cap on the needle and a Teflon plug in the tapered fitting.

The spectra of the sample solutions are recorded from 8.28 to 8.66  $\mu$  with the smallest fixed slit width and highest instrument response compatible with a noise level that is not excessive. The instrument gain is set to produce full scale deflection at the start of a recording.

A standard calibration curve is prepared from pure aldrin samples by the exact procedure outlined above. A base line is drawn from the 8.38  $\mu$  point of the spectrum to the 8.57  $\mu$  point. Distance *A* is measured at 8.48  $\mu$  from the zero radiation line to the base line. Distance *B* is also measured at 8.48  $\mu$  from the zero radiation line to the absorption peak. The ratios *A/B* are correlated for the various standard concentrations of aldrin.

### TOTAL CHLORINE METHOD

See "Chlorine (Total)," p. 1860, and "Chlorine or Bromine in Organic Compounds," p. 1862, below.

## ALLETHRIN<sup>1</sup>

**Reagents.** Ethyl Alcohol, Anhydrous.

Phenolphthalein Indicator, 1% in Methyl Alcohol.

<sup>1</sup> Reproduced with permission from *Analysis of Insecticides and Acaracides*, Interscience Publishers, Inc., New York, 1955.

Sodium Hydroxide 0.02 N—Standardize

Methyl Alcohol Anhydrous

Sodium Hydroxide 0.1 N—Standardize

Hydrochloric Acid 0.1 N Alcoholic Solution—Transfer 17 ml of 6 N hydrochloric acid solution to a 1000 ml volumetric flask and dilute to the mark with methyl alcohol. Standardize by titrating exactly 40 ml with standard 0.1 N sodium hydroxide solution using phenolphthalein indicator.

Morpholine Solution—Transfer 8.7 ml of redistilled morpholine to a reagent bottle and dilute to 1000 ml with methyl alcohol. Fit the bottle with a 2-hole rubber stopper and through 1 hole insert a 20 ml capacity pipet so that the tip extends below the surface of the liquid. Through the other hole insert a short piece of glass tubing attached to a rubber atomizer bulb.

Dimethyl Yellow Methylene Blue Mixed Indicator—Dissolve 10 g of dimethyl yellow (*p*-dimethylaminoazobenzene) and 0.1 g of methylene blue in 125 ml of methyl alcohol.

Pyridine Redistilled

Thymolphthalein Indicator 1.0% in Pyridine

Ethylenediamine (EDA) Redistilled 3% Maximum Water Content

Sodium Methylate Pyridine 0.1 N Solution—Transfer 25 ml of 4 N sodium methylate solution to a reagent bottle containing 75 ml of methyl alcohol and dilute to 1000 ml with redistilled pyridine. Standardize this solution against Bureau of Standards benzoic acid using pyridine as a solvent and thymolphthalein indicator. This reagent readily absorbs carbon dioxide from the air and is best preserved and dispensed from a 50 ml automatic buret. All vents open to the air must have protective Ascarite tubes.

Alpha Naphtholbenzene Indicator 1.0% Solution in Ethyl Alcohol

Potassium Hydroxide 0.02 N Solution in Methyl Alcohol

**Procedure** Determination of Allethrin—Introduce an amount of sample calculated to contain 0.8 to 1.1 g of allethrin into each of two 250 ml glass-stoppered flasks. Reserve 2 additional flasks for blanks and to each of the samples and blanks add 25 ml of redistilled EDA from the buret. Swirl the samples to effect solution. Allow the samples and blanks to stand together at 25° to 30°C for 2 hr.

Unstopper the flasks and wash down the sides of each with 50 ml of redistilled pyridine. To each flask add 6 to 10 drops of the thymolphthalein indicator and titrate with standard 0.1 N sodium methylate solution to the first permanent blue end point.

Determination of Chrysanthemum Monocarboxylic Acid Chloride—Add 8 to 10 drops of dimethyl yellow methylene blue indicator solution to about 150 ml of methyl alcohol in an Erlenmeyer flask. Then add 0.1 N methanolic hydrochloric acid solution dropwise until the mixture appears reddish brown by transmitted light. Add 0.02 N methanolic potassium hydroxide solution dropwise until the appearance of the first green color.

Transfer 25 ml of this green solution to each of three 125 ml glass-stoppered flasks. Reserve 1 of these flasks as a reference blank for the determination of the end point color. Into each of the other flasks introduce with swirling 1.5 to 2.5 g of the sample. Immediately titrate each sample with 0.02 N methanolic potassium hydroxide to the first green end point using the blank as a reference color. Perform this titration within 5 min of the addition of the sample to the methanolic solution.

**Determination of Chrysanthemum Monocarboxylic Acid.**—Transfer 25 ml of anhydrous ethyl alcohol to each of two 125 ml, glass stoppered flasks. Add 8 to 9 drops of alpha-naphtholbenzein indicator solution, and cool the flasks and contents to approximately 0°C in an ice bath. Neutralize the ethyl alcohol in each flask by the dropwise addition of 0.02 *N* sodium hydroxide solution to a brilliant green end point. Introduce 1.5 to 2.5 g of sample into each flask, and immediately titrate with standard 0.2 *N* sodium hydroxide solution to the same brilliant green end point.

**Determination of Chrysanthemum Monocarboxylic Anhydride.**—Carefully pipet 20 ml of the morpholine solution into each of four 250 ml flasks, fill the pipet by exerting pressure in the reagent bottle with the atomizer bulb. Reserve 2 of the flasks for blanks, and introduce 1.5 to 2.5 g of sample into the other 2. Swirl the flasks, and allow the samples and blanks to stand at 25° to 30°C for 5 min. Add 4 to 5 drops of dimethyl yellow methylene blue indicator to each of the 4 flasks and titrate with standard 0.1 *N* alcoholic hydrochloric acid solution until the color changes from green to a faint red, when viewed by transmitted light.

**Calculations.** For *Allethrin*

$$\frac{(T_s - T_b) \times N}{W} = A$$

$$(A + 2B - C - D) \times 30.24 = \text{percentage of allethrin}$$

where  $T_s$  = milliliters of sodium methylate required for the sample,  
 $T_b$  = average milliliters of sodium methylate required for blank,  
 $N$  = normality of sodium methylate solution,  
 $W$  = grams of sample,  
 $A$  = apparent allethrin, milliequivalents per g,  
 $B$  = acid chloride, milliequivalents per g,  
 $C$  = acid-acid chloride, milliequivalents per g, and  
 $D$  = acid chloride-anhydride, milliequivalents per g

For *Acid Chloride*.

$$\frac{T_s \times N}{W} = B$$

$$B \times 18.67 = \text{percentage of acid chloride}$$

where  $T_s$  = milliliters of potassium hydroxide solution required for sample,  
 $N$  = normality of potassium hydroxide, and  
 $W$  = grams of sample

For *Free Acid*.

$$\frac{T_s \times N}{W} = C$$

$$(C - B) \times 16.82 = \text{percentage of free acid}$$

where  $T_s$  = milliliters of sodium hydroxide required for sample,  
 $N$  = normality of sodium hydroxide, and  
 $W$  = grams of sample

For Anhydride

$$\frac{(I_b - T_s) \times N}{W} = D$$

$$(D - 2B) \times 31.84 = \text{percentage of anhydride}$$

where  $I_b$  = average milliliters of hydrochloric acid required for blank

$T_s$  = milliliters of hydrochloric acid required for sample

$N$  = normality of hydrochloric acid and

$W$  = grams of sample

## ALPHA NAPHTHYL THIOUREA

### DETERMINATION IN RODENTICIDES

**Procedure** Weigh a quantity of sample equivalent to approximately 0.2 g of alpha naphthyl thiourea and transfer to a 250 ml Erlenmeyer flask. Add 50 ml of acetone and digest at reflux for 15 min. Filter and wash with acetone. Transfer filtrate to a 500 ml Kjeldahl flask. Place on steam bath and evaporate acetone with an air stream. Determine total nitrogen in the residue by the Kjeldahl method and calculate to alpha naphthyl thiourea using the factor 7.215 times percentage of nitrogen equals percentage of alpha naphthyl thiourea. If much greasy material is present the sample may be digested with a little petroleum ether, filtered on a dry Gooch crucible and washed with petroleum ether. The residue is then heated to 100 C. to remove petroleum ether and the analysis is carried out as indicated above beginning with transfer to a 250 ml Erlenmeyer flask.

## 3 AMINO 1,2,4 TRIAZOLE

### COLORIMETRIC DETERMINATION IN HERBICIDES

**Reagents** Sodium Nitroprusside Solution 5.96 g  $\text{Na}_2\text{Fe}(\text{CN})_5\text{NO} \cdot 2\text{H}_2\text{O}$  in 100 ml

Potassium Ferricyanide Solution 8.44 g  $\text{K}_3\text{Fe}(\text{CN})_6 \cdot 3\text{H}_2\text{O}$  in 100 ml

Sodium Hydroxide Solution 10 g in 100 ml

Hydrogen Peroxide 3%

**Color Reagent**—A few minutes before use mix the reagents above in the proportions 2:2:1:5 respectively and add 1.2 ml of glacial acetic acid for each 100 ml of reagent. This reagent is usable for about one hr.

**Standard Solution**—Dissolve 0.10 g of pure aminotriazole in 100 ml of water.

**Procedure**—Prepare an aqueous solution of the sample and transfer an aliquot containing about 2.5 mg of aminotriazole to a 100 ml volumetric flask. Pipet 2.5 ml of standard solution (2.5 mg of aminotriazole) into a second 100 ml volumetric flask. Dilute the contents of each flask to about 70 ml and add 70 ml of water to a third flask to serve as the blank solution. Add 0.15 ml of 10% sodium hydroxide solution and 10 ml of color reagent to each of the flasks and make to volume. Allow the flasks to stand at room temperature for 2 hr. Filter the solutions if necessary and determine the absorbance of each solution at 634 m $\mu$  against the blank using a suitable spectrophotometer and 1 cm cuvetts.

Calculate the percentage of aminotriazole in the sample from the absorbances and the weight of sample taken.

If  $D$  and  $D_s$  are the optical densities for the sample and standard, and  $W$  and  $W_s$  are the weights used for the sample and standard,

$$\text{Aminotriazole, per cent} = \frac{DW_s(100)}{D_sW}$$

NOTE.—Aminotriazole gives a deep green color, which appears gradually. The blank solution is yellow, but absorbs very little at 634 m $\mu$ .

## ARAMITE

2-(*p*-tert-butylphenoxy) isopropyl-2-chloroethyl sulfite

**Reagents.** Alcoholic Potassium Hydroxide (approximately 1 *N*).

Standard Iodine Solution (0.05 *N*).

Starch Indicator Solution.

**Procedure.**—Weigh a sample containing about 0.35 g. Aramite into a 125-ml., standard tapered Erlenmeyer flask. Add 50 ml. of benzene, stopper, and shake for 1 hr.

NOTE.—Shaking with hexane gives incomplete extraction; hexane may be used with Soxhlet apparatus, however, in place of shaking with benzene.

Transfer a 20-ml. aliquot to a 200-ml., standard tapered Erlenmeyer flask. and evaporate most of the benzene on the hot plate at low heat. Remove from heat, and evaporate the last 3 to 5 ml. with a stream of air, to avoid loss of Aramite. Add 30 ml. of approximately 1 *N* alcoholic potassium hydroxide, and reflux 1 hr. Add about 125 ml. of water, cool in an ice bath, make just acid to phenolphthalein with (1 + 4) sulfuric acid while still cold, and immediately titrate with 0.05 *N* iodine solution, using starch indicator.

Calculate the percentage of Aramite: 1 ml. of 0.05 *N* iodine = 0.00837 g. Aramite.

NOTE.—Sulfur interferes with this method.

## ARSENICALS <sup>2</sup>

### ARSENIC (TOTAL)

**Reagents.** Standard Arsenious Oxide Solution.—Dissolve 2 g. As<sub>2</sub>O<sub>3</sub> in a beaker, by boiling with 150 to 200 ml. of water, containing 10 ml. of sulfuric acid; cool, transfer to a 500-ml. volumetric flask, and dilute to mark.

Standard Iodine Solution.—Mix 6.35 g. of pure iodine with 12.7 g. of pure potassium iodide, dissolve in a small quantity of water, filter, and dilute filtrate to 1 liter in a volumetric flask. Standardize against arsenious oxide solution as follows: pipet 50 ml. of the arsenious oxide solution into an Erlenmeyer flask, dilute to the same volume as that of the aliquot used for titration in the actual determination, neutralize with sodium bicarbonate, add 4 to 5 g. in excess, and add the standard iodine solution from a buret, shaking flask continuously until yellow color disappears slowly from the solution; add 5 ml. of starch indicator, see below, and continue adding the iodine dropwise until a permanent blue color is obtained;

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calculate the value of the standard iodine solution in terms of arsenious oxide and arsenic oxide. To convert arsenious oxide to arsenic oxide multiply by 1.1618. Occasionally restandardize the iodine solution against the standard arsenious oxide solution.

**Standard Bromate Solution**—Dissolve 16.3 g of potassium bromate in water and dilute to 1 liter. One ml of this solution is about equal to 0.003 g of arsenious oxide. Standardize against arsenious oxide solution as follows: pipet 25 ml aliquots of the arsenious oxide solution into 500 ml Erlenmeyer flasks, add 15 ml of hydrochloric acid, dilute to 100 ml, heat to 90°C, and titrate with potassium bromate solution using 10 drops of the methyl orange indicator (see below). Do not add the indicator until near the end of the titration and agitate the liquid continuously to avoid local excess of the potassium bromate solution. Add the potassium bromate solution very slowly when approaching the end of the titration. The end point is shown by change from red to colorless.

**Sodium Hydroxide Solution**—Dissolve 400 g of NaOH in water and dilute to 1 liter.

**Starch Indicator**—Mix about 2 g of finely powdered potato starch with cold water to form a thin paste. Add about 200 ml of boiling water, stirring constantly, and immediately discontinue heating. Add about 1 ml of mercury, shake, and allow starch to stand over mercury.

**Methyl Orange Indicator**—Dissolve 0.5 g of methyl orange in water and dilute to 1 liter.

**Apparatus** See Fig. 39.1. The distilling flask of 500 ml capacity rests on metal gauze that fits over a circular hole in a heavy sheet of asbestos board which

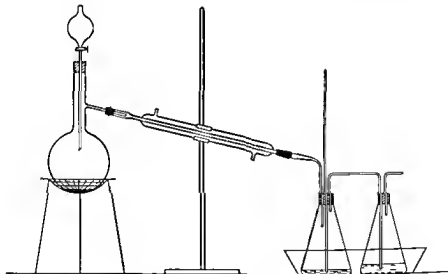


FIG. 39.1 Apparatus for Arsenic Distillation

in turn extends far enough to protect the sides of the flask from the direct flame of the burner. The first receiving flask has a 500 ml capacity and contains 40 ml of water; the second of the same capacity contains 100 ml of water. The volume in the first flask should not exceed 40 ml. Keep both flasks cool with circulating water or ice and water bath.

*Procedure.*—Weigh a quantity of sample containing not more than 0.4 g. of arsenic, and wash it into the distilling flask with 100 ml. of hydrochloric acid. Add 5 g. of cuprous chloride, and distill. When the volume in the distilling flask is reduced to about 40 ml., add 50 ml. of hydrochloric acid from the dropping funnel, and continue distilling, repeating the addition of 50-ml. portions of hydrochloric acid until 200 ml. of acid distillate collects. Wash down the condenser and all connecting tubes carefully, transfer the washings and contents of the Erlenmeyer flasks to a 1-liter volumetric flask, dilute to the mark, and mix thoroughly. Titrate the distillate by one of the following procedures: (a) pipet 200 ml. of the distillate into an Erlenmeyer flask, and nearly neutralize it with the sodium hydroxide solution, using a few drops of phenolphthalein indicator, and keeping the solution well cooled. If the neutral point is passed, add hydrochloric acid until again slightly acid. Neutralize with sodium bicarbonate, add 4 to 5 g. in excess, and add the standard iodine solution from a buret, shaking the flask continuously until the yellow color disappears slowly from the solution. Add 5 ml. of the starch indicator, and continue adding the iodine solution dropwise until a permanent blue color is obtained; (b) pipet a 200-ml. aliquot into an Erlenmeyer flask, and titrate with potassium bromate solution, following the procedure given for standardization of bromate solution, above, beginning with "heat to 90°C. . . ."

From the volume of standard solution used, calculate the percentage of arsenic. Report as arsenious oxide or arsenic oxide, according to the form present in the sample. If the form is unknown, report as arsenic.

This procedure is applicable to the determination of total arsenic in Paris green, lead arsenate, calcium arsenate, zinc arsenite, magnesium arsenite, and arsenicals with Bordeaux mixture, except in the presence of nitrates.

### ARSENIC (WATER-SOLUBLE)

*Reagents.* Standard Iodine Solution.—Prepare and standardize as instructed in procedure for arsenic (total), p. 1849.

Sodium Thiosulfate Solution.—Dissolve 13 g. of crystalline  $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$  in water, and dilute to 1 liter.

Starch Indicator.—Prepare as for arsenic (total), p. 1850.

*Procedure.*—To 2 g. of sample, if powder, or 4 g., if paste, in a 1-liter Florence flask, add 1 liter of recently boiled water that has been cooled to 32°C. Stopper the flask, and place it in a water bath thermostated at 32°C. Digest for 24 hr., shaking hourly for 8 hr. during this period. Filter through a dry filter. If filtrate is not clear, filter again through a Büchner funnel containing paper and a sufficient coating of Filter-Cel to give a clear solution. Discard the first 50 ml. Transfer 250 to 500 ml. of the clear filtrate to an Erlenmeyer flask, add 3 ml. of sulfuric acid, and evaporate on a hot plate. When the volume reaches about 100 ml. add 1 g. of potassium iodide, and continue boiling until the volume is about 40 ml. Cool, dilute to about 200 ml., and add the sodium thiosulfate solution, dropwise, until the iodine color is exactly removed. Avoid the use of starch indicator at this point. Neutralize with sodium bicarbonate and add 4 to 5 g. in excess, titrate with the standard iodine solution until the yellow color disappears slowly, add 5 ml. of the starch indicator, and continue the titration to a permanent blue. Make correction for the quantity of standard iodine solution necessary to produce the same color, using the same reagents and volume. From volume of standard iodine solution used, calculate the percentage of water-soluble arsenic in the sample.

The method is applicable to the determination of water-soluble arsenic in lead

arsenate calcium arsenate zinc arsenite magnesium arsenate and Bordeaux mixture with arsenicals

## CALCIUM ARSENATE

### TOTAL ARSENIC

See Arsenic (Total) p 1849 above

### TOTAL ARSENIOUS OXIDE

Weigh 1 g of sample transfer to a 500 ml Erlenmeyer flask and dissolve in 100 ml of hydrochloric acid (1 + 3) Heat to 90°C and titrate with standard potassium bromate solution as in the method for arsenic (total) From quantity of standard potassium bromate solution used calculate the percentage of arsenious oxide

In the presence of small amounts of nitrates proceed as above except make titration at room temperature

### WATER SOLUBLE ARSENIC

See Arsenic (Water Soluble) p 1851 above

### TOTAL CALCIUM OXIDE

**Reagents** Ammonium Oxalate Solution—Dissolve 40 g of  $(\text{NH}_4)_2\text{C}_2\text{O}_4 \cdot \text{H}_2\text{O}$  in 1 liter of water

**Standard Potassium Permanganate Solution 0.1 N**—Prepared by dissolving 3.2 g of potassium permanganate in 1 liter of water Boil the solution 1 hr Protect it from dust and allow it to stand overnight Thoroughly clean a 15 cm glass funnel a perforated porcelain plate from a Caldwell crucible and glass stoppered bottle (preferably of brown glass) with warm sulfuric acid potassium dichromate solution Digest asbestos for use in Gooch crucibles on a steam bath for 1 hr with about 0.1 N potassium permanganate that has been acidified with a few drops of sulfuric acid (1 + 3) Allow to settle decant and replace with water To prepare the glass funnel place the porcelain plate in the apex make an asbestos pad about 3 mm thick on the plate and wash acid free (Pad should not be too tightly packed and only moderate suction should be applied) Insert the stem of the funnel into the neck of the bottle and filter the potassium permanganate solution directly into the bottle without the aid of suction Transfer 0.3 g (dried 1 hr at 105°C) National Bureau of Standards Standard Sample of sodium oxalate to a 600 ml beaker Add 250 ml of sulfuric acid (5.95) previously boiled for 10 to 15 min and then cooled to about 27°C Stir until the sodium oxalate dissolves Add 39 to 40 ml of the potassium permanganate solution at the rate of 25 to 35 ml per min stirring slowly Let stand until pink disappears (about 45 sec) If pink should persist discard and begin again using a few milliliters less of the potassium permanganate solution Heat to 55 to 60°C and complete the titration by adding the potassium permanganate until a faint pink persists for 30 sec Add the last 0.5 to 1 ml dropwise, with particular care to allow each drop to decolorize before the next is introduced Determine the excess potassium permanganate solution required to impart a pink color to the solution by matching the color obtained by adding potassium permanganate solution to the same volume of the boiled and cooled dilute sulfuric acid at 55 to 60°C This correction is usually 0.03 to 0.05 ml

*Procedure.*—Dissolve a 2 g. sample in 80 ml. of acetic acid (1 + 3), transfer to a 200-ml. volumetric flask, dilute to the mark, and filter through a dry filter. Transfer a 50-ml. aliquot to a beaker, dilute to about 200 ml., heat to boiling, and precipitate the calcium with the ammonium oxalate solution. Let the beaker stand for 3 hr. on a steam bath, filter the solution, and wash the precipitate with hot water. Dissolve the precipitate in 200 ml. of water containing 25 ml. of sulfuric acid (1 + 4), heat to about 70°C., and titrate with the potassium permanganate solution. From the amount of potassium permanganate solution used, calculate the percentage of calcium oxide.

## LEAD ARSENATE

### TOTAL ARSENIC

See "Arsenic (Total)," p. 1849 above.

### TOTAL ARSENIOUS OXIDE

*Procedure.*—Weigh 2 g. of powdered sample, and transfer to a 200-ml. volumetric flask; add 100 ml. of sulfuric acid (1 + 6), and boil for 30 min. Cool, dilute to volume, shake thoroughly, and filter through a dry filter. Nearly neutralize 100 ml. of the filtrate with sodium hydroxide solution as in the method for arsenic (total), and proceed as instructed in that method with titration using standard iodine solution. From volume of standard iodine solution, calculate the percentage of arsenious oxide.

### WATER-SOLUBLE ARSENIC

See "Arsenic (Water-Soluble)," p. 1851 above.

### TOTAL LEAD OXIDE

*Procedure.*—In a porcelain evaporating dish or casserole, on a hot plate, heat 0.5 g. of powdered sample and about 25 ml. of nitric acid (1 + 4). Remove any insoluble residue by filtration. Add 3 ml. of sulfuric acid, and evaporate on a hot plate until the appearance of white fumes. Cool, add a few milliliters of water, and again heat to fuming. Proceed as in the method for lead oxide, below, beginning "Cool, add 50 ml. of water and 100 ml. of alcohol. . . ."

### LEAD OXIDE

*Procedure.*—Weigh 1 g. of powdered sample, and transfer to a beaker. Add 5 ml. of hydrobromic acid (about 1.38 sp. gr.) and 15 ml. of hydrochloric acid, and evaporate to dryness to remove the arsenic. Repeat treatment, add 20 ml. of hydrochloric acid, and again evaporate to dryness. Add 25 ml. of 2 *N* hydrochloric acid to the residue, heat to boiling, filter immediately to remove the silicon dioxide, and wash with boiling water to a volume of 125 ml. All lead chloride should be in solution before filtering; if it will not dissolve completely in 25 ml. of 2 *N* acid, add an additional 25 ml., and dilute the filtrate to 250 ml. Pass in hydrogen sulfide until precipitation is complete. Filter and wash the precipitate thoroughly with 0.5 *N* hydrochloric acid saturated with hydrogen sulfide. Save the filtrate and washings for the determination of zinc, if present. Transfer the paper with the sulfides of lead and copper to a 400-ml. Pyrex beaker, and completely oxidize all organic matter by heating on a steam bath with 4 ml. of sulfuric acid and about 20 ml. of fuming nitric acid in a covered beaker. Evaporate on a steam bath

and then completely remove the nitric acid by heating on a hot plate until copious evolution of white fumes of sulfuric acid occurs. Cool, add 2 to 3 ml of water and again heat to fuming. Cool, add 50 ml of water and 100 ml of alcohol and let stand several hours (preferably overnight). Filter through a Gooch crucible previously washed with water first then with acidified alcohol (100 parts of water 200 of alcohol and 3 of sulfuric acid) and finally with alcohol and dried at 200°C. Wash the precipitate of lead sulfate in the crucible about 10 times with the acidified alcohol and then with alcohol to remove sulfuric acid. Dry at 200°C to constant weight keeping the crucible covered to prevent loss from spattering. From the weight of lead sulfate in the sample calculate the percentage of lead oxide using a factor of 0.7360.

The procedure is applicable to Bordeaux lead arsenate, Bordeaux zinc arsenite, Bordeaux Paris green and Bordeaux calcium arsenate.

## PARIS GREEN

### TOTAL ARSENIOS OXIDE

**Reagent** Ammonium Chloride Solution—Dissolve 250 g of ammonium chloride in water and dilute to 1 liter.

**Procedure**—Weigh 0.3 g of sample and wash into an Erlenmeyer flask with 10 to 15 ml of hydrochloric (1 + 4) or 10 to 15 ml of sulfuric acid (1 + 4) followed by about 100 ml of water and heat on a steam bath only long enough to complete solution at a temperature not exceeding 90°C. (If sulfuric acid is used the solution may be heated to boiling.) Cool, neutralize with sodium bicarbonate, add 4 to 5 g in excess and then add sufficient ammonium chloride solution to dissolve precipitated copper. Dilute somewhat and titrate with standard iodine as for

Arsenic (Total). Make correction for the quantity of iodine solution necessary to produce blue color with starch in the presence of copper using equivalent weight of copper sulfate. From corrected volume of iodine solution calculate the percentage of arsenious oxide.

### WATER SOLUBLE ARSENIOS OXIDE

**Procedure**—To a 1 g sample in a 1 liter Florence flask add 1 liter of recently boiled water that has been cooled to 32°C. Stopper the flask and place it in a water bath thermostated at 32°C. Digest for 24 hr, shaking hourly for 8 hr during this period. Filter through a dry filter and transfer 250 ml of filtrate to an Erlenmeyer flask. Add 4 to 5 g of sodium bicarbonate and titrate with standard iodine solution as in the method for arsenic (water soluble). Correct for quantity of iodine solution necessary to produce the same color using the same reagents and volume. Calculate the amount of arsenious oxide present and express results as percentage of water soluble arsenious oxide.

### TOTAL COPPER OXIDE

**Procedure**—Treat a 2 g sample in a beaker with 100 ml of water and about 2 g of sodium hydroxide. Boil until all of the copper is precipitated as cupric oxide. Filter, wash well with hot water, dissolve the precipitate in hot nitric acid (1 + 4), cool, transfer to a 250 ml volumetric flask and dilute to the mark. Electrolyze a 50 or 100 ml aliquot as instructed in the method for copper below. From the weight of copper calculate percentage of copper oxide.

## COPPER

*Procedure.*—Evaporate the filtrate and washings from the lead sulfate precipitation in the lead oxide procedure to fuming; add a few milliliters of fuming nitric acid to destroy organic matter, and continue the evaporation to about 3 ml. Take up in about 100 ml. of water, add 1 ml. of nitric acid, and filter if necessary. Wash into a weighed, 150-ml. platinum dish, and electrolyze, using a rotating anode and a current of about 3 amp. (A 150-ml. beaker and weighed gauze cathode may be used in lieu of the platinum dish.) After all copper has been deposited (about 30 min.), and while the current is still flowing, wash the deposit with water by siphoning. Interrupt the current, rinse the cathode with alcohol, dry a few moments in an oven, and weigh. Calculate percentage of copper in the sample.

The method is applicable to mixtures of Bordeaux with lead-, zinc-, and calcium-arsenate, and Paris green.

## ZINC ARSENITE

## TOTAL ARSENIC

See "Arsenic (Total)," p. 1849, above.

## TOTAL ARSENIOS OXIDE

Use method for total arsenious oxide, Paris green, using appropriate zinc salt for blank determination.

## WATER-SOLUBLE ARSENIC

See "Arsenic (Water-Soluble)," p. 1851, above.

## TOTAL ZINC OXIDE

*Procedure.*—Transfer to a beaker a 25-ml. aliquot of the solution prepared for acid. If much iron is present, reduce by adding a little sodium bisulfite and heating the determination of total arsenious oxide, above, and add 5 ml. of hydrochloric on a steam bath until the odor of sulfur dioxide has practically disappeared. Cool, dilute to about 100 ml., and proceed with the method for zinc oxide, below, beginning "add 35 to 40 ml. of the mercury-thiocyanate solution reagent. . . ."

## ZINC OXIDE

*Reagent.* Mercury-Thiocyanate Solution.—Dissolve 27 g. of mercuric chloride and 30 g. of ammonium thiocyanate in water, and dilute to 1 liter.

*Procedure.*—Concentrate the filtrate and washings from the sulfide precipitation in the lead oxide procedure, by gentle boiling, to about 50 ml., and continue the evaporation on a steam bath, to dryness. Dissolve the residue in 100 ml. of water containing 5 ml. of hydrochloric acid, and add 35 to 40 ml. of the mercury-thiocyanate solution reagent with vigorous stirring. Allow to stand for at least 1 hr. with occasional stirring. Filter through a weighed Gooch crucible, wash with water containing 20 ml. of the mercury-thiocyanate reagent per liter, and dry to constant weight at 105°C. Weigh and calculate the percentage of zinc oxide, using the factor 0.1633.

to aid in packing. When the boundary between the solvent and silicic acid remains stationary, release pressure cautiously, pipet out most of excess solvent, and reapply pressure until about  $\frac{1}{8}$  in. of solvent remains above adsorbent.

**Procedure.**—Pipet a 10-ml. aliquot of the sample solution onto the column by allowing it to flow slowly down the inside of the column without disturbing the surface of the silicic acid. Wash down the side of the column with 2 ml. of the mobile solvent, and force solution into the silicic acid by applying a 2 to 3 lb. pressure, releasing pressure when all solvent has entered column. Add 10 ml. of mobile solvent, and force into the column. Release pressure and slowly add mobile solvent to within 3 to 5 in. from top of column. Apply sufficient pressure to force solvent through the column at a rate of 3 to 4 ml. per min. Just before the last trace of dye leaves the column, begin to collect 10-ml. fractions, alternately using two 10-ml. graduated cylinders. Transfer each fraction to a 125-ml. Erlenmeyer flask, and evaporate to dryness, using the solvent evaporator. (Fractions should be evaporated without boiling; if boiling occurs, raise flask momentarily from water bath.)

Appearance of gamma isomer will be recognized upon evaporation by its tendency to cover the bottom of the flask as a white residual film with a typical crystal formation. When first residue of gamma isomer is recognized, begin to collect 10-ml. fractions until all gamma isomer is obtained (usually no more than 8 fractions). Dissolve residue in each flask with 5 ml. of *n*-hexane, and transfer to a weighed flask, rinsing flasks successively with 5-ml. portions of *n*-hexane. Evaporate the solvent by using a solvent evaporator. Evacuate the flask about 20 min. at room temperature with a vacuum pump. (There is little danger in evacuating 125-ml. Erlenmeyer flasks; larger size flasks, however, are likely to collapse under vacuum.) Release vacuum, wipe with a clean, moist towel, and allow to stand 5 min. Weigh, and calculate the percentage of gamma benzene hexachloride in the original sample.

**Melting Point Determination of the Gamma Fraction.**—Dissolve the residue in a minimum amount of acetone, and transfer quantitatively to a 10-ml. beaker. Evaporate acetone at 40°C. with the aid of a filtered air stream. Scrape the residue from the beaker for melting point determination. (The beaker may be set on a piece of dry ice to insure the preparation of a finely powdered product.) Place material in an agate mortar, and mix thoroughly with the pestle.

Select 2 clean and dry capillary tubes, and fill with sample. Be sure material is well packed into bottom of tube to insure maximum contact between sample and wall of tube. Insert tubes and thermometer bulb in a Thiele tube so that the samples and the thermometer bulb are contiguous. Start stirrer and heater, and adjust heating rate to 1° per min. at 90°C. Continue heating until the sample melts or 106°C. is reached. Reduce the heating rate to 0.5° per min., and continue heating until sample melts.

The sample melting point is the corrected temperature of the bath when the last solid disappears into the clear melt. If the melting point is less than 108°C., check the result by the infrared method.

#### BENZENE HEXACHLORIDE—TOTAL CHLORINE METHOD

See "Chlorine (Total)," p. 1860, and "Chlorine or Bromine in Organic Compounds," p. 1862, below.

CALCIUM CYANIDE <sup>3</sup>

## CYANIDE

**Reagents.** Soda-Lead Solution.—Dissolve 20 g of lead acetate in water, dilute to 1 liter, and add 200 g of chlorine free sodium carbonate

**Procedure**—Place about 200 ml of water in a 500 ml volumetric flask, and carefully dry the neck of the flask. Weigh about 5 g of sample in a weighing bottle, and transfer to the flask with the least possible exposure to air. Wash the mixture down into the flask and mix by swirling until solution is complete and the small quantity of calcium carbide has been decomposed. Add 25 ml of the soda-lead solution, or a quantity sufficient to remove sulfides, close the flask with a rubber stopper and shake thoroughly, preferably for 30 min. Dilute to the mark, mix and filter through a dry filter. Transfer a 50 ml aliquot to a 400 ml beaker, and proceed as in the method for sodium and potassium cyanides. One ml of 0.1 N silver nitrate equals 0.003204 g of cyanide.  $CN \times 1.7702$  gives percentage of calcium cyanide

CAPTAN <sup>4</sup>

**Reagents** Ammonium Thiocyanate, 0.1 N.

Silver Nitrate, 0.1 N.

Sodium Hydroxide, 0.25 N.

**Procedure**—Weigh 1 g of captan and transfer to a 250 ml, glass stoppered volumetric flask.

Add 125 ml of absolute MeOH and swirl.

Add acetone up to the mark and mix until captan is dissolved. (With technical captan a small flocculent residue may be expected.)

(Do not allow the solution to stand more than 45 min after addition of methanol before proceeding, since captan may slowly react with methanol.) Adjust the volume in the flask as may be necessary because of solvent shrinkage, temperature change, etc. Transfer to a flask suitable for refluxing a 100 ml aliquot. Transfer another 100 ml to an Erlenmeyer flask.

To the portion in the refluxing flask add 50 ml of 0.25 N sodium hydroxide, connect to condenser, and reflux for 1 hr.

After 1 hr refluxing, remove the heat and cautiously add 5 ml of 30% hydrogen peroxide.

When the mixture has cooled somewhat, remove the flask from the condenser, and boil for 10 min to decompose the peroxide and evaporate some solvents. The volume remaining should be about 60 ml. If the solution is not now practically colorless, add 5 ml more hydrogen peroxide (and water if necessary to maintain volume) and boil another 10 min.

Add 10 ml of (1 + 1) nitric acid and about 1 g of ferric sulfate. Add from a buret about 40 ml of standard 0.1 N silver nitrate solution. Add 5 ml of nitrobenzene, shake, and complete Volhard titration. The net titration expressed as milliequivalents gives  $(Cl)_T$ , the total chlorine content of the aliquot.

The titration of the other (untreated) aliquot should be carried out about 45 min. after the solution is begun. The time is not critical, but uniformity of pro-

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<sup>4</sup> Reproduced with permission from the California Chemical Co., Richmond, California.



cedure is desirable. This titration should be done while the other aliquot is refluxing. Proceed as follows: add all at once 60 ml. of the "special reagent solution," the composition of which is given below, and leaving out nitrobenzene, proceed at once with the Volhard titration (about 2 ml. of 0.1 *N* silver nitrate; the titration should be completed within about 2 min. after the "special reagent solution" is added, because captan is hydrolyzed at an appreciable rate under these conditions; the net titration expressed in milliequivalents gives (Cl)<sub>A</sub>, the non-captan chlorine content of the aliquot.

"Special Reagent Solution" for (Cl) Titration.—Make this solution in the proportions of: (1) 50 ml. of water; (2) 10 ml. (1 + 1) of nitric acid; and (3) 1 g. ferric sulfate.

Calculations.—Net captan-chlorine in 100-ml. aliquot

$$(\text{Cl}) = (\text{Cl})_B - (\text{Cl})_A$$

Then, since a 1-g. sample was taken, and the milliequivalent weight of captan is  $\frac{0.3006}{3}$   
 = 0.1002,

$$\begin{aligned}\text{captan, per cent} &= \frac{(\text{Cl}) \times 0.1002}{1 \times \frac{100}{250}} \times 100 \\ &= (\text{Cl}) \times 25.05\end{aligned}$$

## CERESAN AND LIGNASAN

### DETERMINATION OF TOTAL MERCURY

**Reagents.** Mixed Acid.—Place 300 cc. of 20% fuming sulfuric acid in a 500-ml. Erlenmeyer flask; cool in an ice bath, and slowly add 150 ml. of concentrated nitric acid, keeping the acids cold during the mixing.

**Saturated Potassium Permanganate Solution.**

**Saturated Ferrous Alum Solution.**

**Standard 0.05 *N* Ammonium Thiocyanate Solution.**—This solution should be standardized by dissolving 0.25 to 0.3 g. of standard mercuric oxide in 20 to 25 ml. of 1–3 nitric acid, treating with potassium permanganate and ferrous alum, as in the procedure below, and titrating with the ammonium thiocyanate.

**Procedure.**—Weigh a 5-g. sample of ceresan, and transfer it to a dry, 500-ml. Kjeldahl flask. Cool under the tap and add 45 ml. of mixed acid. Place the flask in a "Crisco" or oil bath, put an 8-in. Hopkins condenser in the neck of the flask, and heat the bath to 110°C., and maintain this temperature for 30 min. Then raise the temperature of the bath to 165°C., and keep at this temperature for 1 hr. Remove the condenser, allowing the condensed vapors to drain into the flask. Continue heating for 1 hr. more, remove the flask from the bath, and cool to room temperature under the tap. Add 100 ml. of water,<sup>5</sup> wipe the outside of the flask dry with a cloth, and boil the solution until nearly all the nitrogen oxide fumes have been driven off. Cool the flask under the tap, transfer the contents to a 500-ml. Erlenmeyer flask, and cool again to 20°C. Add saturated potassium permanganate solution until a violet color persists for 5 min. (not less than 5 ml.). Remove the excess potassium permanganate with the ferrous alum solution, and titrate the solution with the ammonium thiocyanate solution to the first permanent pink color.

<sup>5</sup> The water must be free from chlorides; distilled water is preferred.

Calculation    *Standardization*

$$\frac{100 \times \text{weight of HgO}}{\text{milliliters NH}_4\text{CNS} \times 10.83} = N$$

*Determination*

$$\frac{\text{milliliters NH}_4\text{CNS} \times N \times 10.03}{\text{weight of sample}} = \text{percentage of mercury}$$

where  $N$  = normality of  $\text{NH}_4\text{CNS}$  solution

## CHLOROBENZILATE

See Chlorine (Total) below and Chlorine and Bromine in Organic Compounds, p 1862 below

## CHLORINE (TOTAL)

Organic pesticides that contain chlorine may be analyzed by determining the amount of chlorine present and calculating the amount of the pesticide by using the appropriate factor. A partial list of compounds which may be determined in this manner with the factors for conversion of chlorine found to the pesticides follows:

<i>Compound</i>	<i>Factor</i>
Aldrin	1.72
Aramite	9.45
Captan	2.83
Chloranil (Spergon)	1.73
Chlordane	1.56
Chloro-IPC	6.03
DDD, TDE	2.26
DDT	2.00
Dichloro, Phylon	3.20
Dichlorodiethyl ether	2.02
2,4 Dichlorophenoxyacetic acid	3.12
Dieldrin	1.79
Diuron, Karmex DW	3.29
Endrin	1.79
Heptachlor	1.51
Kethane	2.09
Methoxychlor	3.29
Monuron, CMU, Karmex W	5.69
Neotran	3.79
Ovotran	4.28
Pentachlorophenol, technical	1.55
Perthane	4.33
Strobane	1.52
Toxaphene	1.49
2,4,5-Trichlorophenoxyacetic acid	2.40

The factors given are approximate, since technical compounds may contain impurities that contain chlorine. The values will be found to be reasonably accurate for products on the market, and are satisfactory for practical use.

**Reagents.** Benzene, Thiophene Free.

**Ferric Ammonium Sulfate Solution, Saturated.**—This should have sufficient colorless nitric acid to remove the brown color.

**Ferric Sulfate.**

**Nitrobenzene, Mono.**

**Potassium Thiocyanate, Standard Solution, 0.1 N.**

**Silver Nitrate, Standard Solution, 0.1 N.**

**Sodium Metal, Ribbon or Small Pieces.**

**Procedure. Powders.**—Transfer a quantity of sample, containing about 0.5 g. of pesticide, to an extraction thimble, and extract with about 150 ml. of benzene in a Soxhlet extractor for 8 hr. Transfer the benzene extract to a 200-ml. volumetric flask, rinse the extraction flask 2 or 3 times with a few milliliters of benzene, add the rinsings to the volumetric flask, make to volume with benzene, and shake well. Take a 20-ml. aliquot of the diluted benzene extract, transfer to a 300-ml., 24/40 standard taper Erlenmeyer flask, and cautiously evaporate the benzene to about 10 ml. (or slightly less) on a steam bath. Do not let the benzene evaporate to complete dryness. At this point, starting with "Add 50 ml. of 99% isopropanol . . .," follow the procedure given below for liquid formulations.

**Liquid Formulations.**—Transfer a quantity of sample containing about 0.5 g. of pesticide (for compounds containing lower amounts of chlorine, increase to as much as 1.0 g.) into a 100-ml. volumetric flask, add 10 ml. of chlorine- and thiophene-free benzene, and dilute to volume with 99% isopropanol. Mix well and transfer a 10-ml. aliquot of the solution to a 300-ml., 24/40 standard tapered Erlenmeyer flask. Add 50 ml. of 99% isopropanol, 5.0 of freshly cut small pieces of metallic sodium, and shake the flask to mix the sample with the alcohol.

Connect the flask to a reflux condenser and boil gently for 3 hr. If necessary, add more sodium to maintain an excess at all times during the reduction. Shake the flask occasionally. Eliminate excess sodium by cautiously adding 10 ml. of a 1 + 1 mixture of isopropanol and water through the top of the condenser in small portions. Boil for 10 min. more, then slowly add 60 ml. of water. If a cake of solid material has formed on the bottom of the flask, add the first few portions of the 60 ml. of water cautiously, observing closely after each addition for indications of globules of free sodium embedded in the cake. The treatment with 10 ml. of 1 + 1 isopropanol and water does not always dissolve such cakes completely.

Add 5 ml. of 30% hydrogen peroxide, a few drops at a time, through the top of the condenser and boil 15 min. Let cool, add another 5 ml. of 30% hydrogen peroxide, and boil again for 15 min.

Disconnect the flask, add a few glass beads, and boil on the steam bath until the floating layer of benzene and isopropanol has been removed.

Cool, add 2 or 3 drops of 1% phenolphthalein, and neutralize by adding nitric acid (1 + 1) dropwise, then add 10 ml. in excess. Cool, if necessary, to room temperature, transfer contents of the flask and aqueous washings to a small separatory funnel, and shake with 15 ml. of isoamyl alcohol-ether (1 + 1). Drain the aqueous layer into a second separatory funnel, and extract again with 15 ml. of the isoamyl alcohol-ether mixture. Drain the aqueous layer into a 250-ml. beaker. Wash the 2 extracts successively with 10 ml. of water, and repeat with another 10 ml. of water. Combine the aqueous wash solutions with the solution in the beaker.

At this point several procedures for determining the chlorine content of the solution are acceptable. Three choices are listed below.

*Method 1*—Add a slight excess of the silver nitrate solution and coagulate the precipitated silver chloride by digesting on a steam bath for 30 min with frequent stirring. Cool, filter through a fast, qualitative paper, and wash thoroughly with water. Add 5 ml of the ferric alum solution, and determine the excess silver nitrate in the filtrate by titrating with the potassium thiocyanate solution. Subtract the quantity of silver nitrate found in the filtrate from that originally added. The difference is that required to combine with the chlorine in the solution. One ml of 0.1 N silver nitrate = 0.003546 g of Cl.

*Method 2*—Add a slight excess of the silver nitrate solution, then add 5 ml of nitrobenzene and 0.5 g of ferric sulfate, and swirl the flask to coagulate the precipitate. Back titrate the excess silver nitrate with 0.1 N potassium thiocyanate to a faint pink color. Cross titrate with both standard solutions, crossing the end point in each direction, to assure accurate results. Calculate as above.

*Method 3*—The isoamyl extraction step is not required in this procedure. After removal of the isopropanol and benzene from the reaction flask on the steam bath, cool the flask, add 2 to 3 drops of the phenolphthalein solution, neutralize with nitric acid (1 + 1), and add 6 ml in excess. Cool the flask to room temperature and transfer its contents to a 400 ml beaker. The volume should be 200 to 250 ml. Titrate chlorine with 0.1 N silver nitrate potentiometrically, using silver-silver chloride electrodes (Fisher titrimeter or equivalent). Calculate chlorine from amount of silver nitrate required.

**NOTE**—Some formulations may contain benzene soluble colored matter that will interfere with the titration, if done visually. In this case, add to the original benzene solution 0.5 to 1.0 g of decolorizing carbon, and filter through a fast paper into a narrow necked flask, keeping the funnel covered with a watch glass to avoid loss by evaporation. From this point proceed as before. If the potentiometric titration is used, decolorizing is unnecessary.

## CHLORINE OR BROMINE IN ORGANIC COMPOUNDS

### SODIUM BIPHENYL METHOD

This method can be used in place of the sodium reduction method for the determination of chlorine or bromine in organic compounds. The sodium biphenyl reagent is extremely reactive, and rapidly dehalogenates the compound, but it is decomposed by water, alcohols, and acids which may cause the method to fail.

**Reagent** Sodium Biphenyl Reagent—A solution of sodium biphenyl in toluene and ethylene glycol dimethyl ether. It may be prepared by Liggett's method,<sup>6</sup> or purchased from Southwestern Analytical Chemicals.<sup>7</sup>

**Procedure**—Weigh a sample containing 20 to 150 mg of chlorine (35 mg for the potentiometric determination) into a 125 ml or 250 ml separatory funnel containing 20 ml of benzene (chlorine free). For dusts, dissolve the sample in 100 ml of benzene, and take a suitable aliquot for analysis. (Other chlorine free, dry

<sup>6</sup> Liggett, L. M., *Anal. Chem.*, 26, 748 (1954).

<sup>7</sup> Organic halogen reagent (sodium biphenyl solution), Catalogue No. 500, one package approximately \$16.00, from Southwestern Analytical Chemicals, P. O. Box 485, Austin 63, Texas.

solvents, other than alcohols or acids, may be used.) Add 20 ml. of sodium biphenyl reagent (the contents of a bottle of purchased reagent), stopper, and mix, venting the separatory funnel carefully because the contents usually become quite warm. The reaction is complete in 1 or 2 min., and the mixture should have a green or green-brown color, indicating an excess of reagent. If the solution is brown, the reaction may be incomplete, and more reagent must be added; the determination should be abandoned, however, if it is believed that a large quantity of interfering substances is present. Use of a small sample minimizes the interference.

Add water a few drops at a time to decompose the excess of reagent, then add 25 ml. of water, and shake gently to avoid the formation of an emulsion. Transfer the aqueous layer to a second separatory funnel containing 25 ml. of ether, shake, allow to separate, and transfer the aqueous layer to a beaker. Repeat the extraction with two 25-ml. portions of nitric acid (1 + 9), collecting the extracts in the same beaker. The solution should now be acid.

Determine the chloride by potentiometric, gravimetric, or Volhard methods, as in the sodium reduction method.

### CHLORTHION

See "Parathion or Methyl Parathion," p. 1890, and "Phosphorus (Organic)," p. 1891, below.

### CMU

#### 3-(*p*-CHLOROPHENYL)-1,1-DIMETHYLUREA

*Reagents.* Potassium Hydroxide, 20%.

Hydrochloric Acid, 0.1 *N* Standard.

Sodium Hydroxide, 0.1 *N* Standard.

*Apparatus.*—A 500-ml. boiling flask with 24/40 standard-taper joint and thermometer well, with heating mantle and variable transformer. The flask is connected to a vertical reflux condenser, the top of which is connected to the top of a second vertical condenser with a glass U-tube with standard taper joints. The second condenser connects with a glass tube that dips into the solution in a receiving beaker.

*Procedure.*—Weigh a sample containing about 0.4 g. of CMU into the reaction flask, dissolve in 25 ml. of ethyl alcohol, and add 100 ml. of glycerol and 100 ml. of 20% potassium hydroxide. Attach immediately to the first condenser and pipet 50 ml. of 0.1 *N* hydrochloric acid into the receiving beaker. Reflux for 2½ hr. with water flowing in both condensers. Remove the water from the first condenser and distill until the temperature at the thermometer well reaches 175°C. (about 50 min.). The temperature rises rapidly at the end. Titrate the excess standard acid with standard sodium hydroxide potentiometrically, using a glass electrode and a calomel electrode. The inflection point, at about pH 7.6, is taken as the end point. Bromothymol blue may be used as an indicator, and titration may be made visually, with less accuracy. Calculate the percentage of CMU.

1 ml. of 0.1 *N* acid = 0.001987 g. of CMU.

## CRYOLITE

See "Fluorine," below, p 1876

## CUBE

See "Rotenone," below, p 1899

## 2,4-D; 2,4,5-T OR MIXTURES OF BOTH

## TOTAL CHLORINE DETERMINATION

*Procedure*—Weigh and mix 15 g of boric anhydride (Eastman Kodak Co, Catalogue No 2685 or equal) 10 g finely powdered potassium nitrate, and 0.4 g of finely powdered sucrose. Transfer about one fourth of this mixture to a 42 ml Parr bomb, electric ignition type, and add from a small weighing buret about 0.25 to 0.30 g of sample, containing from 0.030 to 0.034 g of chlorine. (If a sample larger than 0.30 g is required use 25 g of boric anhydride. No more than 0.6 g of sample should be used.) Mix well with a thin stirring rod. Add the remainder of the boric anhydride, potassium nitrate, and sucrose mixture in small portions and thoroughly mix after each addition. Measure 15 g of calorimetric grade sodium peroxide in a standard measuring dipper, add a small portion to the contents of the bomb, and stir. Add the balance of the sodium peroxide and thoroughly mix by stirring with the rod. Withdraw the rod and brush free of adhering particles. Quickly cut or break off the lower 15 in. of the rod, and imbed it in the fusion mixture. Sprinkle a small quantity of the sucrose on top of the fusion mixture. Prepare the head by heating the fuse wire momentarily in a flame and immersing it in a small quantity of sucrose. One mg of the sugar is sufficient to start the combustion. Assemble the bomb and ignite it in the usual manner.

Plice about 100 ml of distilled water in a 600 ml beaker, and heat nearly to boiling. After cooling the bomb, dismantle it and dip the cover in the hot water to dissolve any of the fusion that may be adhering to its under side. Wash the cover with a fine jet of distilled water, catching the washings in the beaker. With a pair of tongs, lay the fusion cup on its side in the same beaker of hot water, covering it immediately with a watch glass. After the fused material has been dissolved, remove the cup and rinse with hot water, cool the solution, add several drops of phenolphthalein indicator, neutralize with concentrated nitric acid, and add 5 ml in excess. From this point, the chlorine may be determined by electro-metric titration or by the Volhard procedure.

*NOTE*—The combination of materials used in a sodium peroxide bomb has explosive properties if wrongly handled, and the operator should remain fully aware at all times of the precautions that must be observed and the steps that must be taken to avoid damage to the apparatus and possible personal injury. It is suggested that the instructions and precautions given in the Parr Manual Number 121—Peroxide Bomb Apparatus and Methods, Parr Instrument Company, Moline, Ill. be observed.

This procedure may be used for herbicides containing oils and emulsifiers.

## DDT

COLORIMETRIC METHOD FOR DETECTION IN  
INSECTICIDAL POWDERS

**Reagents.** Nitrating Solution.—A 1:1 mixture by volume of concentrated sulfuric acid and fuming nitric acid.

**Benzene.**

**Sodium Hydroxide Solution, 1%.**

**Sodium Chloride Solution, Saturated.**

**Sodium Methylate Solution, 4 to 5 g. Metallic Sodium per 100 ml. Absolute Methyl Alcohol.**

**Procedure.**—Weigh a quantity of sample, containing about 0.5 mg. of DDT, and transfer it to a large test tube. Add 1 ml. of nitrating solution, immerse in steam bath and heat for 1 hr. Cool, and add 5 ml. of water. Rinse into a small separatory funnel, and extract with 10 ml. of benzene. Wash the benzene extract with 1 or more 10-ml. portions of 1% sodium hydroxide solution, until the washings are colorless. Finally, wash twice with 10-ml. portions of saturated salt solution. To 1 volume of the benzene extract (5 to 10 ml.) add 2 volumes of sodium methylate. *p,p'*-DDT will yield a blue color, *o,p'*-DDT gives a violet red color, and commercial DDT will give a violet blue color.

The method is applicable to mixtures of DDT with sodium fluoride, sodium borate, pyrethrum powder, cubé powder, Lethane A-70, and sulfur. It will give a positive blue color test in the presence of DDD (dichlorodiphenyl-dichloroethane and some aromatic halogen compounds, such as *p*-dichlorobenzene. It is inapplicable in the presence of 2,4-dinitroanisole, which gives a deep orange color, and naphthalene, which gives a red color. The method is not dependable for the detection of DDT in liquid insecticides. Many ingredients in the various formulas, including crude kerosene, cause interference.

## INFRARED DETERMINATION IN DUSTS

**Standard Solution.**—Weigh 0.250 g. technical DDT into a 50-ml. volumetric flask (or other glass-stoppered container) and add exactly 25 ml. of carbon disulfide. If the sample to be analyzed contains sulfur, add the weight of sulfur expected in the portion of sample to be taken for analysis. Shake to dissolve and add a small quantity of anhydrous sodium sulfate. Centrifuge a portion of the solution if it is not clear.

**Procedure.**—Weigh a sample containing about 0.25 g. DDT into a 50-ml. volumetric flask and add exactly 25 ml. of carbon disulfide and a small quantity of anhydrous sodium sulfate. Let stand for at least 30 min. with occasional shaking. Transfer a portion to a glass-stoppered test tube and centrifuge for a short time. Transfer to a sodium chloride cell and scan with an infrared spectrophotometer. Scan the standard solution in the same manner.

Repeat the scan if checking the reproducibility of the instrument is desired.

Measure the absorbance of the DDT peak at  $9.83\ \mu$  with baseline from  $9.4\ \mu$  to  $10.2\ \mu$ , and calculate the percentage of DDT.

## DDT—TOTAL CHLORINE METHOD

See 'Chlorine (Total),' p 1860, and "Chlorine or Bromine in Organic Compounds," p 1862, above

## DEMETON

See Phosphorus (Organic)," p 1891 below

## DERRIS

See "Rotenone," p 1899, below

## DIAZINON

See "Phosphorus (Organic)," p 1891, below

DIBUTYL OXALATE IN INDALONE OR IN 6-2-2  
REPELLENT MIXTURE

*Apparatus* Centrifuge Tubes—These should be oil tubes ASTM, D96 pear shape, 125 ml capacity, graduated to 100 ml, with lower stem graduated to 3 ml in 0.1 ml, or from 0 to 15 ml, in 0.1 ml, from 15 to 5 ml in 0.5 ml, from 5 to 10 ml in 1 ml and also at 15, 20, 25, 50 and 100 ml

*Weighing Sling*—Make a sling from chromel wire to hold centrifuge tube for weighing on analytical balance

*Centrifuge*—The centrifuge must be equipped with Trunnion carrier and head for pear shaped oil tubes

*Shaking Machine*, Fischer Kahn, or Equivalent

*Reagents*. Ethyl Acetate, U S P

Ethyl Alcohol, 95%

Ammonium Hydroxide, C P, Sp Gr, 90

*Oxamide Powder*.—Wash crystalline oxamide with 95% ethyl alcohol, filter on a Buchner funnel, and then wash with ethyl acetate, dry on steam bath to remove solvent completely, and then place in drying oven at 100°C. for 15 min. Transfer the dry powder to a vial

*Procedure*—Place on the tip of a micro spatula a small quantity (about 3 mg) of oxamide powder and transfer to the bottom of a centrifuge tube. Then place the tube in the weighing sling and weigh to the nearest 0.1 mg. Introduce by pipet about 20 ml of sample (Indalone or 6-2-2 repellent mixture) and obtain its weight, by difference to the nearest milligram. Add 40 ml of ethyl acetate and from a buret or pipet, 8 ml of ammonium hydroxide. Stopper the tube tightly, shake vigorously by hand for about 15 sec, and remove the stopper to release the pressure, stopper and repeat the shaking for 15 sec, release the pressure, finally stopper tightly, place the tube in the shaking machine, and fix firmly in a horizontal position. Shake mechanically for 30 min, and remove the tube. Place in the centrifuge immediately and centrifuge for 5 min at about 2000 rpm. Remove the tube, and at once decant the liquid carefully from the precipitate in the stem of the tube. Add about 5 ml of 95% ethyl alcohol, and wash the precipitate by



carefully rocking and rotating the tube in the palms of the hands. Using about 5 ml. of 95% ethyl alcohol, wash down the walls of the tube. Centrifuge at 2000 r.p.m. for 5 min., again decant carefully, and repeat the above washing operation, using ethyl acetate instead of ethyl alcohol. Centrifuge finally for 5 min., and decant carefully. By gently tapping the stem of the tube against the palm of the hand, and rotating the tube, disperse the precipitate along the lower wall of the tube. Now place the tube in a horizontal position on the steam bath and heat 5 min. or more until traces of ethyl acetate are removed, as determined by absence of odor. Place the tube in a drying oven at 100°C. for 15 min., remove, allow to cool to room temperature, and weigh. Calculate the percentage of dibutyl oxalate as follows:

$$\text{Dibutyl oxalate, per cent} = \frac{W_p}{W_s} \times 230$$

where  $W_p$  = weight of precipitate in grams, and  
 $W_s$  = weight of sample in grams.

## DIELDRIN

### DETERMINATION IN FORMULATIONS BY PARTITION CHROMATOGRAPHY

*Reagents.* Silicic Acid, Mallinckrodt's Chromatographic Grade.

Ethyl Ether.

*n*-Hexane, Technical, Redistilled.

Nitromethane, Redistilled.

Petroleum Ether.

Mobile Solvent.—*n*-Hexane saturated with nitromethane.

Mixed Dye Solution.—Dissolve 25 mg. each of D and C Violet No. 2 and D and C Red No. 18 in 50 ml. of mobile solvent. Store in a glass-stoppered bottle.

*Apparatus.*—Chromatographic tube, as specified for determining gamma BHC.

*Preparation of Sample.*—Weigh a sample of dust containing 1.00 g. of dieldrin, and extract on Soxhlet or Goldfish for 6 hr. or overnight. If DDT is present the sample should be limited to contain 1 g. or less of DDT. Evaporate the extract until the ether odor is not detected. Add 25 ml. of mobile solvent, and on dusts containing sulfur, heat just to boiling. Allow to cool to room temperature. Decant through pea-sized wad of cotton into a 50-ml. volumetric flask containing 1 ml. of the mixed dye solution. Make a second hot extraction on the sulfur bearing dusts. On other dusts, transfer the residue from the ether extract to a 50-ml. volumetric flask with mobile solvent. Add 1 ml. of mixed dye, and make to volume.

For 16% dieldrin solutions, weigh a 4-g. sample into a 50-ml. volumetric flask, add 1 ml. of mixed dye, and make to volume with mobile solvent. Some samples contain materials that go through the column and prevent good separation of fractions; if this happens weigh the required amount of sample into a 125-ml. Erlenmeyer flask. Add a few boiling stones and 10 to 20 ml. of petroleum ether "F." Attach to a suction manifold, and place in a warm water bath. Too much suction will cause a sudden boiling and loss of sample. Leave on suction in the bath until the volume no longer decreases. Repeat this several times, if possible,

until a solid residue is obtained. Take this residue up with mobile solvent and prepare sample as usual.

**Preparation of the Column**—For all samples except dieldrin in oil solutions use 75 g ( $\pm 0.5$  g) of silicic acid about 42 ml of nitromethane and 225 ml of mobile solvent. Because each batch of silicic acid is different the amount of nitromethane required must be determined by trial. For dieldrin in oil samples use 100 g of silicic acid about 55 ml of nitromethane and 300 ml of mobile solvent. Transfer to a Waring Blendor mix for 15 sec and then pour mixture quickly into the chromatographic tube. A 3 ft glass stirring rod worked around in the tube will remove trapped air bubbles. Apply pressure to the column until the silicic acid ceases to settle. Release the pressure and remove all except 1 in of the upper solvent layer using steady suction and a trap to catch the solvent. Again apply pressure up to 8 lbs to the column until about  $\frac{3}{8}$  in of mobile solvent remains above the silicic acid. (The silicic acid should remain covered with mobile solvent if the top of the column becomes dry channeling may occur.)

**Operation of the Column** Pipet 10 ml of the prepared sample solution and allow to flow slowly down the side of the tube. Force solution into the silicic acid. Wash wall twice with 1 to 2 ml portions of mobile solvent pressing each washing into the column then gently fill the tube up to within 1 in of the top with mobile solvent. Apply pressure to give a flow to 3 to 4 ml per min.

**Collection of the Fractions**—For samples containing DDT in addition to dieldrin collect the fractions from just before the red band reaches the fritted disc through all the red portion. This contains the DDT. Between the red band and the violet band is the hexachloro epoxy octahydro dimethanonaphthalene (HEOD). Start taking fractions for this when all of the red dye is out of the column taking 5 ml fractions until the HEOD appears. Evaporate these fractions carefully as the material tends to splatter. Splattering may be eliminated by using a steam bath and no suction instead of a water bath at 65°C and reduced pressure. Combine fractions in a weighed flask, evaporate on water bath at 60° to 65°C using reduced pressure cautiously, and finally evaporate at room temperature with a high vacuum pump. Calculate the percentage of hexachloro epoxy octahydro dimethanonaphthalene in the sample.

### DIELDRIN—TOTAL CHLORINE METHOD

See Chlorine (Total) p 1860 and Chlorine or Bromine in Organic Compounds p 1862 above.

### N,N-DIETHYL *m* TOLUAMIDE

The technical product Delpheene contains about 85% meta isomer of diethyl toluamide and other isomers. If alcohol is present it must be removed prior to infrared analysis since it absorbs strongly in the 13  $\mu$  to 15  $\mu$  region.

**Standard Solution**—Weigh 0.4 g of pure diethyl *m* toluamide into a 10 ml volumetric flask and make to volume with carbon disulfide.

**Procedure**—Weigh a sample containing about 0.4 g of diethyl *m* toluamide into a 125 ml Erlenmeyer flask and evaporate the alcohol at about 50°C under vacuum on a rotary evaporator. Do not heat longer than necessary. Transfer the residue to a 10 ml volumetric flask and make to volume with carbon disulfide. Add anhydrous sodium sulfate and shake to remove any water. The solution should be clear.

Transfer to a sodium chloride cell, and scan the sample solution and the standard solution using the following settings for the Perkin-Elmer model 21 spectrophotometer:

Cell:	0.5 mm., compensated with CS <sub>2</sub>
Range:	13 $\mu$ to 15 $\mu$
Resolution:	960 (program)
Speed:	2
Gain:	adjusted

Measure the absorbance of the meta isomer peak at 14.15  $\mu$ , and, with the base point at 14.44  $\mu$ , calculate the percentage of diethyl-*m*-toluamide.

## DIPHACINONE

### SPECTROPHOTOMETRIC METHOD FOR PRODUCTS CONTAINING ABOUT 0.005% DIPHACINONE (2-DIPHENYLACETYL-1,3-INDANDIONE)

**Reagents.** Sodium Pyrophosphate, 1%.—Dissolve 5 g. of Na<sub>4</sub>P<sub>2</sub>O<sub>7</sub>·10H<sub>2</sub>O in 500 ml. of water.

**Petroleum Ether, Purified.**—Extract 200 ml. of petroleum ether 3 times with 20-ml. portions of 1% sodium pyrophosphate.

**Procedure.**—Weigh 20 g. of sample into a Soxhlet thimble, and extract with ethyl ether for 4 hr. Evaporate the extract to less than 50 ml. on the steam bath, transfer to a 50-ml. volumetric flask, and make to volume with ethyl ether. Pipet 2 ml. into a glass-stoppered, 16- by 150-mm. test tube. add 10 ml. of 1% sodium pyrophosphate solution with a pipet, stopper, and shake vigorously for 2 min. Centrifuge at high speed until the aqueous layer is clear. Draw off the ether layer by means of an aspirator connected to a tube drawn out to a fine tip. Add 2 ml. of ether, shake vigorously, centrifuge, and draw off the ether layer. Repeat with a second 2 ml. of ether, and then repeat twice more with 2-ml. portions of petroleum ether, purified.

Prepare a blank solution in the same manner using 2 ml. of ethyl ether in place of the 2 ml. of ether extract.

Determine the absorbance (*A*) of the aqueous solution at 286 m $\mu$  in a 1-cm. silica cuvet.

**Calculation.**—

$$\text{Diphacinone, per cent} = A(.0113)$$

**NOTE.**—The absorption curves for Diphacinone and Pival are similar, but the principal peak for Diphacinone is at 286 m $\mu$ , and for Pival, at 283 m $\mu$ . Since these peaks are rather strong, a maximum at 286 m $\mu$  indicates that Diphacinone rather than Pival is present, in the absence of strong interference.

## DISODIUM ENDOTHAL IN FORMULATIONS

**Reagents.** Standard Sodium Hydroxide, 0.1 *N*.

Standard Sulfuric Acid, 0.1 *N*.

**Procedure.**—Weigh a sample containing about 0.4 g. of disodium endothal into a platinum dish, and neutralize carefully with 0.1 *N* sulfuric acid using phenolphthalein indicator.

**NOTE**—If ammonium sulfate is present add 1 g of sodium hydroxide to the sample in the platinum dish and evaporate to dryness. Dissolve in water, and exactly neutralize with sulfuric acid (finishing with 0.1 N), and proceed with the method.

Evaporate and ash the sample, extract with hot water, and filter through filter paper into a 500 ml Erlenmeyer flask, washing with water. Return the filter paper to the platinum dish, and ash completely. Dissolve the residue in water, and add it to the Erlenmeyer flask. Add 50 ml of standard 0.1 N sulfuric acid, and boil 20 min to remove carbon dioxide. Cool, and titrate with standard 0.1 N sodium hydroxide to the phenolphthalein end point.

Calculation.—

$$\text{Disodium endothal, per cent} = \frac{V(0.11507)(100)}{W}$$

where  $W$  = weight of sample, and

$V$  = volume of 0.1 N sulfuric acid consumed

## DIURON

### DICHLOROPHENYL DIMETHYL COMPOUND

See Fenuron," p 1872 below. Calculate the percentage of dichlorophenyl dimethylurea as follows

$\text{Cl}_2\text{C}_6\text{H}_3\text{NHCON}(\text{CH}_3)_2$ , per cent

$$= \frac{\left\{ \begin{array}{l} \text{[(milliliters of 0.1 N HCl} \times V) \\ - (\text{milliliters of 0.1 N NaOH} \times N)] \times 23.31 - A \end{array} \right\}}{\text{sample weight (grams)}}$$

where  $A$  = total amines as TMA HCl  $\times 2.4389$

## DN COMPOUNDS\*

This method may be used for a number of insecticides and acaricides including dicyclohexyl ammonium 4,6 dinitro 2 cyclohexylphenate (DN 111), 2 Methyl-4,6 dinitrophenol (DNC), and 2 Cyclohexyl 4,6 dinitrophenol (DNOCHP)

**Reagents.** Ethyl Alcohol, 95%

**Potassium Cyanide Solution**—Dissolve 40 g of potassium cyanide in distilled water, and dilute to 100 ml. Prepare fresh daily.

**Procedure**—To 1 g of powdered sample in a 25 ml Erlenmeyer flask add 5 ml of water, 2 ml of ethyl alcohol, and allow to stand at 20°C for 65 min. Add 5 ml of 40% freshly prepared, potassium cyanide solution. Stir a moment, filter through a dry, fritted glass crucible into a dry flask. This is the check sample.

Simultaneously with the above procedure, treat an identical sample in an identical manner except that the potassium cyanide solution is added just prior to the 65 min period, instead of just after it. The transmittancy is determined at 540 mμ, using the check sample to set the instrument.

A standard calibration curve is prepared from the pure DN compound using the exact analytical procedure as is used for the samples.

\* Reproduced with permission from Analysis of Insecticides and Acaricides. Interscience Publishers, Inc., New York, 1935.

## ENDRIN

See "Chlorine (Total)," p. 1860, and "Chlorine or Bromine in Organic Compounds," p. 1862, above.

## EPN

See "Phosphorus (Organic)," p. 1891, below.

## 2-ETHYL-1,3-HEXANEDIOL

*Reagents.* Acetylating Reagent.—One volume ACS acetic anhydride and 3 volumes reagent pyridine, preferably freshly redistilled.

*Mixed Indicator.*—One part 0.1% cresol red, neutralized with NaOH, and 3 parts 0.1% thymol blue, neutralized with NaOH.

*Standard Alcoholic Sodium Hydroxide 0.5 N.*—Prepare from 50% NaOH solution and aldehyde-free ethanol or c.p. methanol. Standardize against potassium acid phthalate.

*Procedure.*—Weigh a sample containing about 0.7 g. of 2-ethyl-1,3-hexanediol into a 300-ml. iodine flask, and add 10 ml. acetylating reagent with a pipet. Run a blank determination in the same manner, without the sample. Stopper the flask and moisten the glass stopper with pyridine. Heat on the steam bath for at least 1 hr., using the maximum heat that is practical. Cool, add 10 ml. of water by way of the well, and mix to bring the water in contact with all the reagent. Add a few drops of mixed indicator and titrate with 0.5 N alcoholic NaOH solution.

*Calculation.*—

$$\text{percentage} = \frac{NV(.07311)(100)}{W} = \frac{NV}{W} (7.311)$$

where  $V$  = milliliters of NaOH solution for the blank, less the milliliters of NaOH solution used for the sample,

$N$  = normality of the NaOH solution, and

$W$  = weight of sample.

## ETHYLENECHLOROBROMIDE

See "Methyl Bromide," p. 1883, below.

## ETHYLENE DIBROMIDE

See "Methyl Bromide," p. 1883.

## ETHYLENE DICHLORIDE

See "Chloride (Total)," p. 1860, and "Chlorine or Bromine in Organic Compounds," p. 1862, above.

ETHYLENE OXIDE<sup>9</sup>

**Reagents** Magnesium Chloride, Saturated Solution—Add 10% sodium hydroxide solution until magnesium hydroxide precipitates then filter

Hydrochloric Acid 10 N Solution—Standardize before use

Sodium Hydroxide, 10 N Solution—Standardize before use

Methyl Orange Indicator, 0.1% Solution

**Procedure**—A known volume of the saturated neutral solution of magnesium chloride is pipetted into a 300 ml Erlenmeyer flask equipped with a ground glass stopper. An ampoule containing a weighed amount of ethylene oxide is carefully introduced into the flask which is then stoppered and shaken vigorously to break the ampoule. The mixture is allowed to stand for 6 hr at room temperature. The liberated magnesium hydroxide is determined by adding excess standard 10 N hydrochloric acid solution and back titrating to the methyl orange end point with standard 10 N sodium hydroxide solution.

Calculate as follows

$$\frac{(A_m - B_m) \times 4.4}{W} = \text{percentage of ethylene oxide}$$

where  $A_m$  = milliliters of 10 N hydrochloric acid solution

$B_m$  = milliliters of 10 N sodium hydroxide solution and

$W$  = grams of sample

FENURON<sup>10</sup>

## ASSAY BY BASIC HYDROLYSIS

**Reagents** Standard 0.1 N Hydrochloric Acid

Standard 0.1 N Sodium Hydroxide

Glycerol USP or CP

Potassium Hydroxide CP 20% Aqueous Solution

Silicone Defoamer (Dow Corning Antifoam A Midland Mich.)

**Procedure**—Accurately weigh  $0.7 \pm 0.01$  g of sample (40 g for ground pellets) and transfer quantitatively to a clean dry reaction flask of the hydrolysis apparatus. See Fig. 39.2

**NOTE**—A number 5 glossine powder paper (Eli Lilly and Co.) is satisfactory for weighing and quantitatively transferring the powder sample to the reaction flask.

Add 15 ml of methyl alcohol and swirl to completely disperse the sample warning gently if necessary.

Add 100 ml of glycerol several drops (6 to 8) of silicone defoamer 1 or 2 boiling chips and 100 ml of 20% potassium hydroxide solution.

**NOTE**—For ground pellets it may be necessary to use up to 5 ml of defoamer in order to control the excessive tendency to foam.

<sup>9</sup> Reproduced with permission from *Analysis of Insecticides and Acaricides* Interscience Publishers Inc. New York 1955.

<sup>10</sup> Furnished by the Methods Clearing House Committee of the Association of American Pesticide Control Officials Inc.

Immediately attach the reaction flask to the assembled hydrolysis apparatus, having first added 50 ml. of 0.1 *N* hydrochloric acid, accurately measured from a buret, and a like volume of methanol to the absorption trap.

With cooling water flowing through each condenser, independently, heat the contents of the reaction flask to boiling by means of the heating mantle, and maintain reflux conditions for a period of 3½ hr., or until the solution clears.

Remove cooling water from condenser *A* to start distillation, and continue the hydrolysis and distillation until the pot temperature reaches 175°C. Adjust the heating rate so that this temperature is attained and distillation is completed in 1½ to 2½ hr. Then turn cooling water into condenser *A*, and turn off the power. *Caution.*—It is essential that the joint between the 2 condensers be broken immediately when the heater is shut off and the cooling water is admitted to condenser *A*; any suck-back into the reaction flask would result in a violent eruption.

Rinse condenser *B* and the connecting tube with methanol, followed by distilled water, adding the rinsings to the beaker trap.

Titrate the contents of the beaker with 0.1 *N* sodium hydroxide solution, using a pH meter with glass-calomel electrode system, and determine the end point by differential method, corresponding to the milliliters required coinciding with the second derivative equal to zero. Record the titration to the nearest 0.01 ml.

*NOTE.*—For routine analysis, titrate the contents of the beaker trap using a Beckman Model K automatic titrator, with anticipation switch at 5 and delivery tip in position A (see manufacturer's instruction bulletin). Titrate to a pH setting of 6.8, and the differential technique needs to be used only for occasional checking purposes or for the most accurate determinations.

Calculate the percentage of phenyl dimethylurea by the following formula:

$C_6H_5NHCON(CH_3)_2$ , per cent

$$= \frac{[(\text{Mls } 0.1 \text{ } N \text{ HCl} \times N) - (\text{Mls } 0.1 \text{ } N \text{ NaOH} \times N)] \times 16.42 - A}{\text{sample weight (grams)}}$$

where *A* = total amines as DMA HCl  $\times 2.014$ .

### FERBAM <sup>11</sup>

*Apparatus.* Hydrolysis Apparatus and Absorption Train.—See Fig. 39-3.

*Reagents.* Alcoholic Potassium Hydroxide.—Prepare by adding 112 g. of reagent

<sup>11</sup> Furnished by the Methods Clearing House Committee of the Association of American Pesticide Control Officials, Inc.

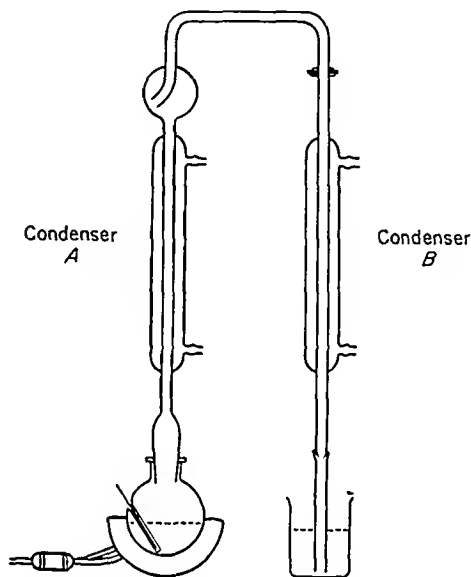


FIG. 39-2. Apparatus for Basic Hydrolysis.

grade potassium hydroxide pellets to 1 liter of anhydrous methanol Use a methanol grade meeting the following specifications methanol 99.8% minimum acetone 0.003% maximum acetic acid 0.003% maximum

Standard 0.1 N Iodine Solution

Lead Acetate Solution 10%

Acetic Acid 30% Solution

Starch Indicator Solution

Phenolphthalein Indicator Solution

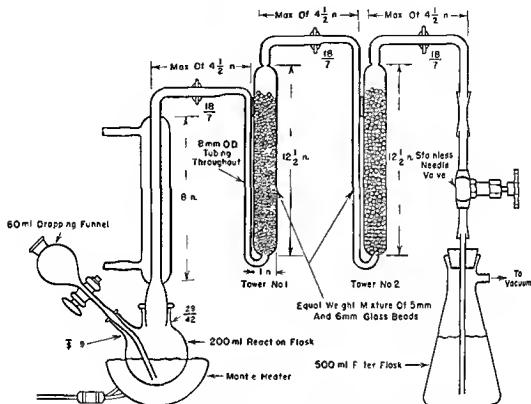


FIG. 39.3 Distillation Apparatus for Dithiocarbamate Distillation

**Versene Liquid**—A 34% solution of the tetrasodium salt of ethylenediamine tetraacetic acid

**Procedure**—Using a graduated cylinder add 10 ml of 10% lead acetate solution to the first absorption tower and 25 ml of alcoholic potassium hydroxide solution to the second tower. It is essential that the second tower be perfectly clean and dry before the alcoholic potassium hydroxide is added. The use of acetone or anhydrous methanol as drying agents is recommended.

Thoroughly clean and dry the dropping funnel and reaction flask and assemble the absorption train according to Fig. 39.3 insuring against leaks by the application of lubricant to each joint.

Accurately weigh a sample of 0.6 to 0.7 g and transfer quantitatively to the dry reaction flask then add 10 ml of Versene Liquid and swirl the contents of the flask for 15 to 20 sec or until the ferrous is completely dispersed. There is a



slow decomposition of the ferbam in the alkaline "Versene" so there should be a minimum delay between the additions of "Versene" and the hot digestion acid. However, the sample should be completely dispersed in the "Versene" before proceeding.

Attach the reaction flask, and insert the dry dropping funnel, positioning it so that the bent delivery tube is pointing downward. Adjust the vacuum so that a rapid stream of bubbles is drawn through the metering water trap.

Add 50 ml. of nearly boiling distilled water, followed immediately with 50 ml. of nearly boiling 9 *N* (1 + 3) sulfuric acid. The initial reaction may be quite rapid and the acid should be added slowly to avoid any "back-up" of evolved carbon disulfide into the dropping funnel. It may be necessary to increase the vacuum somewhat at this point. If at any time there is the slightest evidence of carbon disulfide "back-up" into the dropping funnel, it is necessary to discard the determination entirely and start anew.

After all the acid has been added, allow the stopcock of the dropping funnel to remain open long enough for a few bubbles of air to be drawn up through the contents of the flask for mixing, then adjust the stopcock to a partially opened position, place the preheated mantle heater under the flask, and bring the reaction mixture to a boil.

Cautiously adjust the vacuum to reduce the bubble rate to about 3 bubbles per sec., and continue refluxing, maintaining the reaction mixture at reflux temperature for 90 min., during which time the bubble rate is maintained at about 3 bubbles per sec. Adjust the dropping funnel stopcock as necessary to maintain proper pressure relationships throughout the train, and to provide an air sweep to transport the evolved gases.

At the completion of the digestion period, disassemble the absorption train and wipe the joints of the second (alcoholic potassium hydroxide) trap clean with tissue. *Caution.*—Do not remove the heat from the reaction flask until the absorption train has been disconnected, in order to prevent suck-back of solutions in the absorption towers.

Quantitatively transfer the contents of the second tower to a 500-ml. Erlenmeyer flask, using 200 ml. of distilled water in approximately 8 equal portions. After adding each portion of rinse water, the packed tower should be tipped and agitated repeatedly in order to insure adequate washing of the bead surfaces. The tip of the tower, through which the contents are poured, should always be maintained in the mouth of the Erlenmeyer flask to avoid losses of the xanthate solution during transfer.

Add one drop of phenolphthalein indicator to the xanthate solution contained in the 500-ml. flask, and carefully neutralize the excess potassium hydroxide by the addition of 30% acetic acid solution, added from a buret. *Caution.*—Do not add excess acid at this point because the potassium methyl xanthate is unstable in a strongly acid medium.

Immediately titrate the neutralized xanthate solution with standard 0.1 *N* iodine solution, adding the solution rapidly until the end point is approached (as evidenced by the slow disappearance of the brown color). Add a 5-ml. portion of starch indicator solution, measured from a graduate, to the solution, and titrate to the usual blue starch-iodine end point. The equivalence point is taken at the point where the blue coloration of the end point persists for at least 15 sec. The entire titration should be completed in 2 min. or less.

Determine the standard 0.1 N iodine solution blank by titrating the alcoholic potassium hydroxide water phenolphthalein and acetic acid solution mixtures in the same proportion as added in the procedure.

Calculate the percentage of ferbam by the following formula

$$\text{Ferbam per cent} = \frac{(A - B) \times N \times 13.8835}{\text{sample weight (grams)}}$$

where  $A$  = milliliters of 0.1 N iodine in the determination titration

$B$  = milliliters of 0.1 N iodine in the blank titration and

$N$  = normality of 0.1 N iodine

**NOTE 1** Studies have indicated that the length of time necessary to obtain complete decomposition of the sample is probably considerably less than 1½ hr. A period 1½ hr has been used to date however and it is recommended that the time be maintained at this period since the accuracy and reproducibility cited is obtainable under these conditions.

**NOTE -2** The 0.1 N iodine solution should be standardized frequently against National Bureau of Standards arsenious oxide. Store the solution in a dark bottle.

## FLUORINE<sup>12</sup>

### LEAD CHLOROFLUORIDE METHOD

**Reagents** Fusion Mixture—Mix anhydrous sodium carbonate and potassium carbonate in equi molecular proportion.

**Lead Chlorofluoride Wash Solution**—Dissolve 10 g of lead nitrate in 200 ml of water dissolve 1 g of sodium fluoride in 100 ml of water and add 2 ml of hydrochloric acid mix these 2 solutions. Allow precipitate to settle and decant supernatant liquid. Wash 4 or 5 times with 200 ml of water by decantation and then add about 1 liter of cold water to the precipitate and allow to stand 1 hr or longer with occasional stirring. Pour through a filter and use the clear filtrate. By adding more water to the precipitate of lead chlorofluoride and stirring more wash solution may be prepared as needed.

**Standard Silver Nitrate Solution 0.2 N**—Standardize by titration against pure sodium chloride using potassium chromate indicator.

**Standard Potassium or Ammonium Thiocyanate Solution 0.1 N**—Standardize by comparing with the standard solution of silver nitrate under the same conditions that are pertinent in the determination.

**Ferric Indicator**—Add to cold saturated water solution of ferric alum (free from Cl) sufficient colorless nitric acid to bleach the brown color.

**Bromophenol Blue Indicator**—Grind 0.1 g of the powder with 15 ml of 0.1 N sodium hydroxide and dilute to 25 ml.

**Procedure**—Mix 0.5 g (or less if necessary to make content of fluorine fall between 0.01 and 0.1 g) of sample (dried at 105°C) with 6 g of fusion mixture and 0.2 to 0.3 g of powdered silica and heat to fusion over a Bunsen burner. (Use of blast lamp is not required as it is necessary only that the mass be fluid and it is preferable not to heat much beyond the temperature at which it melts. If much aluminum is present a uniform clear liquid melt cannot be obtained. There

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will be particles of a white solid separated in the liquid. The melt, after cooling, should be colorless, or, at least, should not have more than a gray color.) Leach cooled melt with hot water, and filter when disintegration is complete. Return the insoluble residue to a platinum dish by the use of a jet of water, add 1 g. of sodium carbonate, make the volume 30 to 50 ml., boil for a few minutes, disintegrating any lumps with a glass rod flattened on the end, filter through the same paper, wash thoroughly with hot water, and adjust the volume of filtrate and washings to approximately 200 ml. Add 1 g. of zinc oxide dissolved in 20 ml. of nitric acid (1 + 9), boil 1 min. with constant stirring, filter, and wash thoroughly with hot water. During this washing return the gelatinous mass to the beaker once or twice, and thoroughly disintegrate it in the wash solution, because it is difficult to wash this precipitate on the filter. (The mass can easily be returned to the beaker by rotating the funnel above the beaker, and at the same time cutting the precipitate loose from the paper with a jet of wash solution.)

Add 2 drops of bromophenol blue, and then nitric acid nearly to neutrality, leaving solution slightly alkaline. Boil solution gently with the cover glass on the beaker, to expel carbon dioxide. Finally add nitric acid (1 + 4) until color just changes to yellow. Remove from burners, add dilute sodium hydroxide until the color just changes to blue, and add 3 ml. of 10% sodium chloride solution. The volume of the solution at this point should be 250 ml.

Add 2 ml. of hydrochloric acid (1 + 1) and 5 g. of lead nitrate, and heat on a steam bath. As soon as the lead nitrate is in solution, add 5 g. of sodium acetate, stir vigorously, and digest on a steam bath 30 min. with occasional stirring. Allow to stand overnight at room temperature. Decant the solution through a paper of close texture; wash precipitate, beaker, and paper once with cold water, then 4 or 5 times with a cool saturated solution of lead chlorofluoride, and then once more with cold water.

Transfer the precipitate and paper to the beaker in which precipitation was made, stir the paper to a pulp, add 100 ml. of nitric acid (5 + 95), and heat on a steam bath until the precipitate is dissolved (5 min. is ample to dissolve this precipitate. If sample contains an appreciable quantity of sulfates the precipitate will contain lead sulfate, which will not dissolve. In such a case, heat 5 to 10 min. with stirring, and consider the lead chlorofluoride to be dissolved). Add a slight excess of 0.2 *N* silver nitrate solution, digest on a steam bath for 30 min., cool to room temperature while protected from light, filter, wash with cold water, and determine silver nitrate in the filtrate by titration with the standard thiocyanate solution, using 5 ml. of the ferric indicator. Subtract the quantity of silver nitrate found in the filtrate from that originally added. The difference will be that required to combine with the chlorine in the lead chlorofluoride, and from this difference, calculate the percentage of fluorine in the sample on the basis that 1 ml. of 0.2 *N* silver nitrate = 0.00380 g. of fluorine.

NOTE.—This method gives accurate results for quantities of fluorine between 0.01 and 0.10 g. Below 0.01 g., the results have a tendency to be slightly low, and above 0.1, slightly high. Satisfactory results are obtained in the presence of boron and aluminum. This method should be used for all samples of fluorides that contain kaolin or Fuller's earth as a filler.

If the sample contains appreciable quantity of sulfur, it should be removed with carbon disulfide and fluorine, determined on air-dry residue, allowance being made in calculations for the percentage of sulfur removed.

## FLUORINE PRESENT AS SODIUM FLUOSILICATE

**Reagents** **Alcoholic Potassium Chloride Solution**—Dissolve 60 g of potassium chloride in 400 ml of water add 400 ml of alcohol and test with phenolphthalein. If solution is not neutral adjust to exact neutrality by the addition of sodium hydroxide or hydrochloric acid solution.

**Alcoholic Potassium Chloride and Sodium Carbonate Solution**—Dissolve 1 g sodium carbonate in 100 ml of the alcoholic potassium chloride solution.

**Standard Sodium Hydroxide Solution**—Approximately 2 N prepared in manner to assure absence of carbonate and standardized.

**Procedure**—Weigh a 1 g sample into a platinum dish and add rapidly with continuous stirring 50 ml of the alcoholic potassium chloride sodium carbonate solution. Do not allow the solution to become acid and if necessary use a larger quantity of the reagent to insure alkalinity. Continue stirring until all soluble portions of the sample have dissolved. Filter through a Gooch crucible containing a disc of filter paper covered with a medium pad of asbestos. Wash the precipitate with the alcoholic potassium chloride solution until 1 washing does not destroy the color made by 1 drop of 0.2 N sodium hydroxide and phenolphthalein (3 to 4 washings are usually sufficient). Transfer the crucible and contents to a 400 ml beaker add 100 ml of recently boiled water and 1 to 2 ml of 1% phenolphthalein solution heat and titrate with the standard sodium hydroxide. Finish titrating with the fluoride solution actively boiling. Calculate the percentage of sodium fluosilicate on the basis that each milliliter of 0.2 N sodium hydroxide is equal to 0.009403 g of sodium fluosilicate.

## FORMALDEHYDE (IN SOLUTIONS)<sup>13</sup>

**Reagents** **Sulfuric Acid**—Normal. Prepare and standardize by approved procedure.

**Sodium Hydroxide Solution**—Normal. Standardize against sulfuric acid using litmus or bromothymol blue indicator. 1 ml is equal to 30.03 mg of formaldehyde.

**Hydrogen Peroxide Solution**—Commercial containing about 3% H<sub>2</sub>O<sub>2</sub>. If acid neutralize with the sodium hydroxide solution using litmus or bromothymol blue indicator.

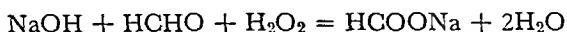
**Litmus Indicator**—A solution of purified litmus of such concentration that 3 drops will impart a distinct blue color to 50 ml of water.

**Bromothymol Blue Indicator**—Dissolve 1 g of bromothymol blue in 500 ml of alcohol 70% by volume.

**Procedure**—Measure 50 ml of the sodium hydroxide solution into a 100-ml Erlenmeyer flask and add 50 ml of the hydrogen peroxide. Add a weighed quantity of sample (about 3 g) allowing the point of the weighing pipet to reach nearly to the liquid in the flask. Place a funnel in the neck of the flask and heat on a steam bath for 5 min shaking occasionally. Remove from the steam bath wash the funnel with water cool the flask to room temperature and titrate the excess sodium hydroxide with normal acid using the bromothymol blue or litmus indicator. (It is necessary to cool the flask before titration to obtain a sharp end

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point with litmus.) From the quantity of normal sodium hydroxide used, calculate the percentage of formaldehyde according to the following equation:



If the formaldehyde solution contains appreciable free acid, titrate a separate portion and make correction for this acidity.

### FUMARIN

3-(Alpha-acetonylfurfuryl)-4-hydroxycoumarin)

#### SPECTROPHOTOMETRIC METHOD FOR PRODUCTS CONTAINING ABOUT 0.5% FUMARIN IN CORNSTARCH

*Reagents.* Sodium Pyrophosphate Solution, 1%.—Dissolve 5 g.  $\text{Na}_4\text{P}_2\text{O}_7 \cdot 10\text{H}_2\text{O}$  in 500 ml. of water.

Petroleum Ether, Purified.—Extract 200 ml. of petroleum ether 3 times with 20-ml. portions of 1% sodium pyrophosphate solution.

*Procedure.*—Weigh a 0.6-g. sample into a 125-ml., glass-stoppered flask, and add 50 ml. of ethyl ether with a pipet. Shake on a shaking machine for at least 30 min. Centrifuge, if necessary, to clarify the solution. Pipet 2 ml. into a glass-stoppered, 16- by 150-mm. test tube, add 10 ml. of 1% sodium pyrophosphate solution with a pipet, stopper, and shake vigorously for 2 min. Centrifuge at high speed until the aqueous layer is clear. Draw off the ether layer, including any emulsion that remains, by means of an aspirator connected to a tube drawn out to a fine tip. Add 2 ml. of ether, shake vigorously, centrifuge, and draw off the ether layer. Repeat using 2 ml. of petroleum ether (purified).

Prepare a blank solution in the same manner, using 2 ml. of ethyl ether in place of the extract.

Add a sufficient quantity (about 3 ml.) to a 1-cm. silica cuvet, and determine the absorbance at 305  $\text{m}\mu$ .

*Calculation.*—

$$\text{Fumarin, per cent} = \text{absorbance} \times 0.896$$

Norr.—The spectrophotometric curves for fumarin and warfarin are very similar, but warfarin has a peak at 308  $\text{m}\mu$ , and fumarin has a peak at 305  $\text{m}\mu$ . In products such as 0.5% concentrates in cornstarch, which does not interfere, fumarin and warfarin may be distinguished by determining the wavelength of the absorption peak.

### GENITE

See "Chlorine (Total)," p. 1860, and "Chlorine or Bromine in Organic Compounds," p. 1862, above.

### GUTHION

See "Phosphorus (Organic)," p. 1891, below.

## HEPTACHLOR IN TECHNICAL HEPTACHLOR AND FORMULATIONS

**Reagents.** **Standard Silver Nitrate Solution (0.1 N).**—Dissolve 17 g of silver nitrate in 125 ml of distilled water and 25 ml of concentrated nitric acid, and dilute to 1 liter with glacial acetic acid. Standardize against the sodium chloride solution using the titration given in the procedure.

**Standard Sodium Chloride Solution (0.1 N).**—Dissolve 5.845 g of pure sodium chloride in 1 liter of water.

**Procedure.**—Weigh a sample, containing between 200 and 350 mg of heptachlor into a 250 ml, standard taper Erlenmeyer flask. Add 25 to 50 ml of glacial acetic acid and warm gently, if necessary, to dissolve the heptachlor. Add 25 ml of the standard silver nitrate solution with a pipet, and reflux for 45 min.

Cool and quantitatively wash the contents of the flask into a 400 ml beaker using 80% acetic acid and adjust the volume to about 300 ml. Titrate the excess  $\text{AgNO}_3$  with the standard sodium chloride solution potentiometrically, using a silver electrode, a glass electrode, and a magnetic stirrer.

Using the Fisher titrimeter set the potential at 0.50 at the start. The end point is at about 0.27 and the change in potential is very sharp.

**Calculation.**—The volume of sodium chloride solution corresponding to the sample is the volume equivalent to 25 ml of standard silver nitrate solution minus the titration. Calculate the percentage of heptachlor as 1 ml 0.1 N  $\text{NaCl}$  = 0.03733 g heptachlor.

## LIGNASAN

See 'Ceresan and Lignasau,' p 1859, above

## LINDANE

See 'Benzene Hexachloride,' p 1856, above

## MALATHION<sup>14</sup>

The method is applicable to dusts, dust base concentrates, and wettable powders, where malathion is the only active ingredient. Other extractable organic materials, such as dispersing agents, emulsifiers, and solvents, may interfere, and should be tested for interference. Sulfur does not interfere.

**Apparatus.** **Infrared Spectrophotometer.**—This should be capable of making measurements in the 11 to 13  $\mu$  range. Use a 0.5 mm cell for 4 to 10% dusts, and a 0.1 mm cell for 25 to 50% products.

**Reagents.** **Malathion Standard Solution.**—Accurately weigh 0.2 to 0.25 g of purified malathion (for 4 to 10% dusts), or 1.2 to 1.25 g (for 25 to 50% dust base concentrates and wettable powder) into a 2 oz bottle fitted with a screw cap with vinylite liner. Add from a pipet or buret 25 ml of acetonitrile, and shake well.

**Acetonitrile.**—Essentially transparent to 11 to 13  $\mu$  region.

**Procedure.**—Accurately weigh a 5 g sample (for 4 to 5% dust or 25% dust base

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concentrate or wettable powder), or 2.5 g. (for 10% dust or 50% dust base concentrate). Transfer quantitatively to a 2-oz., wide-mouth bottle fitted with screw cap with vinylite liner. Add from a pipet or buret 25 ml. of acetonitrile, and shake well about 2 min. Filter through Whatman No. 12 folded paper into a glass-stoppered flask, and stopper.

Fill a suitable cell, using a hypodermic syringe, with the appropriate standard solution, and obtain infrared spectrum from 11.0 to 13.0  $\mu$ . Using the same instrument settings, scan the sample solutions in the same manner.

Measure distances  $Y$  and  $X$  for both sample and standard, where  $X$  is the distance from the zero line to the peak at 12.2  $\mu$ , and  $Y$  is the distance from the zero line to the base line at an 11.45  $\mu$  valley. Calculate absorbance,  $A$ , of each solution as follows: absorbance =  $\log (Y/X)$ .

Malathion, per cent

$$= \left( \frac{A_{\text{sample}}}{A_{\text{standard}}} \right) \left( \frac{\text{weight of standard}}{\text{weight of sample}} \right) \times \text{percentage of purity of standard}$$

See "Phosphorus (Organic)," p. 1891, below.

### MANEB<sup>15</sup>

("Manzate" Maneb Fungicide)

The method given for Ferbam may be used for Maneb, the only difference being in the factor used in calculation. Calculate the percentage of manganese ethylene bis-dithiocarbamate as follows:

$$\text{Maneb, per cent} = \frac{(A - B) \times N \times 13.265}{\text{sample weight (grams)}}$$

where  $A$  = milliliters of 0.1  $N$  iodine in determination titration,

$B$  = milliliters of 0.1  $N$  iodine in blank titration, and

$N$  = normality of 0.1  $N$  iodine.

### MERCURY

#### DETERMINATION IN PANOGEN 15 AND PANOGEN 42

*Reagents.* Solid Potassium Nitrate.

Hydrogen Peroxide, 3%.

Potassium Permanganate, 0.3  $N$ .

Potassium Thiocyanate, 0.05  $N$ .

*Ferric Alum Indicator.*—Dissolve 35 g. of ferric alum in 100 ml. of distilled water and 20 ml. of 6  $N$  nitric acid.

*Procedures.*—Weigh out samples of the Panogen from a small weighing bottle into 500-ml. Erlenmeyer flasks, covering the flask after addition of the Panogen. (Use about 0.5 g. for Panogen 15 and 0.25 g. for Panogen 42.) To the flask containing the Panogen, add 15 ml. of concentrated nitric acid, 10 ml. of concentrated sulfuric acid, and solid potassium nitrate (3 to 4 g. for Panogen 15 and about

<sup>15</sup> Furnished by the Methods Clearing House Committee of the Association of American Pesticide Control Officials, Inc.

10 g for Panogen 42) Add a few boiling beads and heat over a full flame. If the material darkens, add a small amount of solid potassium nitrate and continue heating. If the liquid darkens again, add solid potassium nitrate in small amount until the boiling mixture is colorless or pale yellow. Continue boiling to the appearance of dense white fumes. Allow to cool, and then dilute (cautiously) with about 50 ml of distilled water.

Again heat to boiling, add 0.3 N potassium permanganate solution dropwise until a violet color persists and continue boiling for several minutes. Cool and add dropwise 3% hydrogen peroxide until the solution becomes colorless. Usually only 1 drop of the peroxide is needed. Now add about 3 ml of ferric alum indicator and titrate with 0.05 N potassium thiocyanate solution to the appearance of a distinct brown tint.

Calculation —

$$\text{Mercury, per cent} = \frac{\text{milliliters of KSCN} \times \text{normality of KSCN} \times 10.03}{\text{sample weight}}$$

Methylmercury dicandamide per cent

$$= \frac{\text{milliliters of KSCN} \times \text{normality of KSCN} \times 14.9}{\text{sample weight}}$$

## MERCURY

### DETERMINATION OF VERY SMALL QUANTITIES IN MIXTURE WITH ORGANIC MATERIAL

**Reagents** Fuming Sulfuric Acid (20%)

Fuming Nitric Acid

Saturated Potassium Permanganate

Hydroxylamine Hydrochloride Solution, 20 g per 100 ml

**Dithizone Solution**—Dissolve 130 mg of diphenylthiocarbazone in 500 ml of carbon tetrachloride, let stand 1 day in the dark, filter, and store in the dark. 1 ml should be equivalent to 0.01 to 0.005 mg of mercury.

**Mercury Standard Solution**—Dissolve 500 mg of mercury in nitric acid, dilute to 500 ml. Take 10 ml of this solution and 10 ml of nitric acid, and make up to 1 liter, 1 ml of solution is equivalent to 0.0100 mg of mercury.

**Procedure**—Transfer a sample, containing about 1 mg of mercury, to a 250 ml Erlenmeyer flask with a 24/40 interchangeable joint, add 10 ml of sulfuric acid and mix. Connect to a water-cooled, reflux condenser and add 20 ml of fuming sulfuric acid and a small quantity of fuming nitric acid. Heat gently, adding more fuming nitric acid if necessary until the sample is decomposed (no longer chars) and in absence of chlorides heat for 15 min more. In the presence of chlorides continue the heating for 2 hr. Slowly add 100 ml of water through the condenser while cooling the flask. Transfer to a beaker, dilute to 200 ml, and boil 1 min to remove most of the nitrous oxide. Add a saturated solution of potassium permanganate to about a 4 ml excess and cool to room temperature. Remove the excess with hydroxylamine hydrochloride solution. Filter if necessary, and make up to a 250 ml volume.

Transfer 20 or 50 ml to a 250 ml separatory funnel, and dilute to 100 ml. Add



5 ml. of hydroxylamine hydrochloride solution, shake, let stand a few minutes, and add 0.5 to 1.0 g. of c.p. sodium chloride.

**Titration.**—Add 2 to 3 ml. of dithizone solution, and shake until the carbon tetrachloride layer is bright orange (about 20 shakes). Allow to separate, draw off the lower layer, and discard. Continue adding smaller amounts of dithizone solution toward the end. If the end point is overstepped (green or brownish yellow color), add a known quantity of the mercury standard solution, and continue the titration. The end point is reached when 0.1 ml. of dithizone solution gives a green color that remains after 60 shakes.

Standardize the dithizone solution by titrating against 10 ml. of the mercury standard solution, which is equivalent to 0.10 mg. of mercury. The 10 ml. of the mercury standard solution is transferred to a 250-ml. separatory funnel, diluted to 100 ml., and the hydroxylamine hydrochloride and sodium chloride are added as directed in the procedure.

Run a blank using all the reagents specified in the method, deduct it from the titration obtained with the aliquot, and calculate the percentage of mercury in the sample.

**NOTE.**—The quantities of acids used may be reduced, or another method may be used if only a small quantity of organic matter is present. The normality of the solution to be titrated should be less than 1.0 *N* in acid.

The solution titrated should contain about 0.1 to 0.2 mg. of mercury.

## METHOXYCHLOR

See "Chlorine (Total)," p. 1860, and "Chlorine and Bromine in Organic Compounds," p. 1862, above.

## METHYL BROMIDE

**Reagents.** Sodium Acid Phosphate.

Hypochlorite Solution, 1 *N* in 0.1 *N* Sodium Hydroxide Solution.

Sodium Formate, 50% Solution.

Sodium Molybdate, 1% Solution.

Potassium Iodide.

Sulfuric Acid, 6 *N* Solution.

Sodium Thiosulfate, 0.1 *N* Solution.—Stabilize with 1 g. of sodium carbonate per 1000 ml. Standardize against 0.1 *N* potassium iodide solution in the presence of 75 ml. of water, 10 ml. of 6 *N* sulfuric acid solution, and 0.5 g. of potassium iodide per aliquot of thiosulfate solution being titrated.

Starch Indicator, 1% Solution.

**Procedure.**—Follow the sodium-isopropanol reduction procedure for "Chloride (Total)," p. 1860, to the point where peroxide has been added and the solution has been boiled. Cool the solution, and make slightly acid with 6 *N* hydrochloric acid, then neutralize with dilute sodium hydroxide solution, adjusting to the color change of methyl red. Adjust the volume at this point to about 150 ml.

About 2 g. of sodium acid phosphate and 5 ml. of hypochlorite solution are now added, and the mixture is heated to boiling. After a minute or so, 5 ml. of the sodium formate solution are introduced, and boiling is continued for 2 min. The sample is cooled and treated with a few drops of 1% sodium molybdate solution,

0.5 g of potassium iodide and 25 ml of 6 N sulfuric acid solution. Titration should be made immediately with standard 0.1 N sodium thiosulfate solution adding starch indicator just before the end point. A blank on all the reagents should be carried through the entire procedure.

Calculate as follows

$$\frac{(T_s - T_b) \times 1.583}{W} = \text{percentage of methyl bromide}$$

where  $T_s$  = milliliters of 0.1 N sodium thiosulfate used for sample,

$T_b$  = milliliters of 0.1 N sodium thiosulfate used for blank, and

$W$  = grams of sample

### METHYL PARATHION

See Parathion or Methyl Parathion p 1890 below

### MONURON

#### CHLOROPHENYL DIMETHYL COMPOUND

See Fenuron p 1872 above. Calculate the percentage of chlorophenyl dimethylurea as follows

$\text{ClC}_6\text{H}_4\text{NHCON}(\text{CH}_3)_2$ , per cent

$$= \frac{\left\{ \begin{array}{l} \text{[(milliliters of 0.1 N HCl} \times N) \\ - \text{(milliliters of 0.1 N NaOH} \times N)] \times 19.865 - A \end{array} \right\}}{\text{sample weight (grams)}}$$

where  $A$  = percentage of total amines as TMA  $\text{HCl} \times 2.0785$

### NABAM<sup>16</sup>

(Parzate Soda Salt Solution)

The method given for Ferbam may be used for Nabam, the only difference being in the factor used in calculation. Calculate the percentage of sodium ethylene bisdithiocarbamate as follows

$$\text{Na}_2\text{EBD per cent} = \frac{(A - B) \times N \times 12.818}{\text{sample weight (grams)}}$$

where  $A$  = milliliters of 0.1 N iodine in determination titration,

$B$  = milliliters of 0.1 N iodine in blank titration, and

$N$  = normality of 0.1 N iodine

### NEBURON<sup>17</sup>

*Apparatus* Distillation Apparatus—As shown in Fig. 39-4

*Reagents* Sulfuric Acid, Concentrated

<sup>16</sup> Furnished by the Methods Clearing House Committee of the Association of American Pesticide Control Officials Inc.

<sup>17</sup> Furnished by the Methods Clearing House Committee of the Association of American Pesticide Control Officials Inc.

Hydrochloric Acid, 0.1 *N*.

Sodium Hydroxide, 0.1 *N*.

Antifoam A Emulsion (Dow Corning).

**Procedure.**—A large sample of the urea to be analyzed is finely ground in a mortar, and a subsample is taken for determination. A 4.0 g. sample of the formulation is accurately weighed and transferred to a test tube. The sample is washed into the bottom of the tube with 20 ml. of concentrated sulfuric acid. The test tube is then placed in an oil bath at 170°C. for 5 min., after which it is removed and allowed to cool to room temperature. The contents of the tube are transferred to the 500-ml., round bottom flask of the distilling apparatus, using 100 ml. of distilled water. A few boiling chips are added along with 1 ml. of anti-foam, and the apparatus is assembled.

A trap containing standard 0.1 *N* hydrochloric acid is placed in position, with the delivery tube just below the surface of the acid, and 100 ml. of 30% sodium hydroxide are then added through the funnel. Heat is applied, and the solution is brought to a rapid boil.

When 180 ml. of the distillate have been taken over, the heat is removed, and the condenser and delivery tube are rinsed down with distilled water.

The contents of the trap are titrated to a potentiometric end point with 0.1 *N* NaOH, using a Beckman Model K automatic titrator, with anticipation switch at 5 and the delivery tip in position A (see manufacturer's instruction bulletin).

Calculation.—

Neburon, per cent

$$= \frac{[(\text{milliliters of acid} \times N) - (\text{milliliters of NaOH} \times N)] \times 27.5178 - A}{\text{sample weight}}$$

where *A* = percentage of total amines as methyl *n*-butyl amine hydrochloride  $\times 2.2259$ .

## NICOTINE<sup>18</sup>

**Reagent. Silicotungstic Acid Solution.**—Dissolve 120 g. of silicotungstic acid ( $4\text{H}_2\text{O} \cdot \text{SiO}_2 \cdot 12\text{WO}_3 \cdot 22\text{H}_2\text{O}$ ) in water, and dilute to 1 liter. The acid should be white or pale yellow crystals, free from green color, and the solution should be free from cloudiness and green color. Do not use any of the several other silicotungstic acids.

<sup>18</sup> Reproduced with permission from "Official Methods of Analysis," Association of Official Agricultural Chemists, Inc., Washington, D. C.

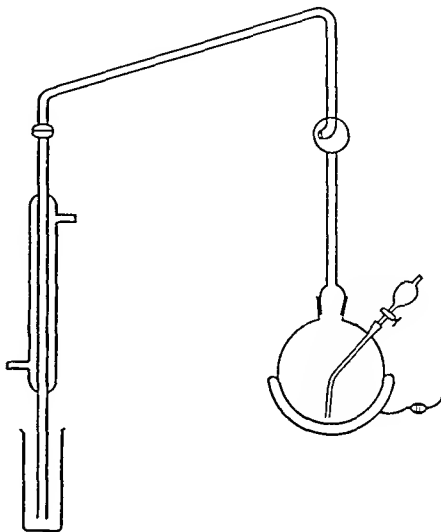


FIG. 39-4. Distillation Apparatus.

**Procedure**—Weigh a quantity of the sample that will contain preferably 0.1 to 1.0 g of nicotine. If the sample contains very little nicotine do not increase the quantity to a point where it interferes with the distillation. Wash into a 500 ml Kjeldahl flask with water and if necessary add a little paraffin to prevent fothing and a few small pieces of pumice to prevent bumping. Add 10 g of sodium chloride and 10 ml of sodium hydroxide solution (30% by weight) and close flask with a rubber stopper through which passes the stem of a trap bulb and an inlet tube for steam. Connect the trap bulb to a well cooled condenser the lower end of which dips below the surface of 10 ml of hydrochloric acid (1 + 4) in a suitable receiving flask. Steam distil rapidly. When the distillation is well under way heat the flask to reduce the volume of liquid as far as practicable without bumping or undue separation of insoluble matter. Distil until a few milliliters of distillate show no cloud or opalescence when treated with a drop of the silicotungstic acid solution and a drop of hydrochloric acid (1 + 4). Confirm the alkalinity of the residue in the distilling flask with phenolphthalein indicator. Make the distillate which may amount to 1000 to 1500 ml to convenient volume. (The solution may be concentrated on a steam bath without loss of nicotine.) Mix well and pass through a dry filter if not clear. Test the distillate with methyl orange to confirm acidity. Pipet an aliquot containing about 0.1 g of nicotine into a beaker. (If samples contain very small quantities of nicotine an aliquot containing as little as 0.01 g of nicotine may be used.) To each 100 ml of solution add 3 ml of hydrochloric acid (1 + 4) and 1 ml of silicotungstic acid solution for each 0.01 g of nicotine supposed to be present. Stir thoroughly and let stand overnight at room temperature. Before filtering stir the precipitate to see that it settles quickly and is in crystalline form. Filter on either ashless paper or a Gooch crucible and wash with hydrochloric acid (1 + 1000) at room temperature. Continue washing for 2 or 3 fillings of filter after no more opalescence appears when a few milliliters of fresh filtrate are tested with a few drops of nicotine distillate. In the case of paper transfer paper and precipitate to a weighed platinum crucible dry carefully and ignite until all carbon is destroyed. Finally heat over a Meker burner no more than 10 min. The weight of residue multiplied by 0.1141 equals the weight of nicotine present in the aliquot. In the case of the Gooch crucible dry in an oven for 3 hr at 105°C and weigh. Weight of residue times 0.1012 equals the weight of nicotine present in the aliquot.

### ORGANIC THIOCYANATES

This procedure determines organic thiocyanates by determining their nitrogen content using the Kjeldahl method. The method is applicable to Lethane 384 Lethane 60 Lethane 384 Special and Thanite.

**Reagents** Sulfuric Acid 0.10 N

Sodium Hydroxide, 0.10 N

**Sodium Hydroxide Solution**—This consists of 450 g of commercial NaOH free from nitrates in 1 liter of water.

**Sulfide Solution**—This consists of 40 g of sodium or potassium sulfide in 1 liter of water.

**Procedure**—Weigh 4 to 5 g of the sample and transfer to an 800 ml Kjeldahl flask. Add 15 to 18 g of anhydrous potassium or sodium sulfate 0.7 g of mercuric oxide and 35 ml of concentrated sulfuric acid. Let stand for 15 min with occa-

sional shaking, then apply heat, gently at first, but gradually raising the temperature as the reaction quiets down, until gentle boiling is attained. Continue boiling until the contents of the flask have been colorless for at least 1 hr. Avoid heating any dry part of the flask and, if necessary, add more acid, observing the quantity added. From this point, follow the standard Kjeldahl procedure, and determine the quantity of nitrogen present in the aliquot used.

Factors for calculating the percentage of active ingredient and the percentage of base ingredients are given below. Since the Lethane bases are about 50% active ingredient, by volume, and Thanite is 82% isobornyl thiocynoacetate, factors for both the active ingredients and the bases are given.

Multiply the percentage of nitrogen determined by the factor given for determining the percentage of the particular organic thiocyanate present.

Lethane 384 base	14.573
Lethane 384	26.739
Lethane 60 base	21.263
Lethane 60	38.242
Lethane 384 Special base	19.185
Lethane 384 Special	34.506
Thanite	22.054
Isobornyl thiocynoacetate	18.084

## ORGANIC THIOCYANATES

### IN SPRAY MATERIALS

**Reagents.** Polysulfide Solution.—Dissolve 180 g. of potassium hydroxide in 120 ml. of water. Saturate 100 ml. of this solution with hydrogen sulfide (about 42 g.) while cooling. Add the other 100 ml. of potassium hydroxide solution and 80 g. of sulfur. Shake until dissolved.

Sodium Sulfide ( $\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$ ).

Mixed Sulfide Solution.—To 100 ml. of polysulfide solution, add 50 g. of sodium sulfide, 30 g. of potassium hydroxide, and 200 ml. of water.

Sodium Bisulfite.

Sulfur Dioxide.

Copper Sulfate Solution, (20%  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ ).

Potassium Hydroxide Solution, 10%.

Sulfuric Acid (1 + 4).

Wash Solution.—To 300 ml. of water add 1 ml. of sulfuric acid, 1 g. of sodium bisulfite, 10 ml. of copper sulfate solution, 12 g. of sodium sulfate, and pass sulfur dioxide into the solution for 10 min.

**Procedure.**—Weigh a quantity of sample, preferably containing about 0.03 g. of thiocyanate nitrogen, into a 250-ml., glass-stoppered Erlenmeyer flask. (If the percentage is very low, the weighed quantity should not be increased unduly without correspondingly increasing the quantity of mixed sulfide solution used; 20 to 25 g. of fly spray is usually sufficient.) Add 35 ml. of the mixed sulfide solution. Shake vigorously at room temperature for 10 min., during which time reaction is nearly completed. Heat to 70°C. on a steam bath, carefully releasing the pressure resulting from heating, and shake at the temperature of 70°C. for 15 min. or more. Cool.

indicator, and titrate with 0.1 *N* hydrochloric acid to the change from green to yellow.

Carry through the same procedure a blank determination on exactly 5 ml. of the standard potassium hydroxide solution.

Calculations.—

$$\frac{(A_b - A_s) \times 3.032}{W} = \text{percentage of } p\text{-chlorophenyl-}p\text{-chlorobenzenesulfonate}$$

where  $A_b$  = milliliters of 0.1 *N* hydrochloric acid required for blank sample,

$A_s$  = milliliters of 0.1 *N* hydrochloric acid required for sample, and

$W$  = grams of sample.

NOTE.—Phenols will interfere unless determined separately. Free phenols may be determined by extracting the residue, after removal of the ether solvent, with water or dilute alkali, followed by an appropriate phenol determination on the aqueous extract.

## PANOGEN

### DETERMINATION OF METHYL MERCURY DICYANDIAMIDE

*Reagents.* Saturated Solution of Potassium Permanganate.

Oxalic Acid Solution (1 *N*).—Dissolve 6.3 g. of oxalic acid in sufficient water to measure 100 ml.

Ferric Ammonium Sulfate.—Dissolve 8 g. of ferric ammonium sulfate in sufficient water to measure 100 ml.

Ammonium Thiocyanate, 0.1 *N*.

*Procedure.*—Transfer a sample containing approximately 0.1 g. of mercury to a 800-ml. Kjeldahl flask. Place in an ice bath, and cautiously add 8 ml. of concentrated sulfuric acid, insert a small funnel into the neck of the flask, then add slowly 10 ml. of nitric acid. Remove the flask from the ice bath and allow it to stand at room temperature for 15 min. with occasional shaking. Heat the mixture, at first gently on a steam bath, then more strongly over a burner, until the solution is colorless or only slightly yellow, adding more nitric acid if necessary, and keeping the funnel in the neck of the flask during the heating. Allow the solution to cool sufficiently, and cautiously add through the funnel about 50 ml. of cold water, rinsing the stem of the funnel with a few milliliters of water, and allowing the rinsings to run into the flask. Add saturated potassium permanganate solution to the warm solution dropwise, until a slight pink color persists. Discharge the pink color by the addition of just sufficient oxalic acid solution. Cool the solution, add 3 ml. of nitric acid and 2 ml. of ferric ammonium sulfate, and titrate with 0.1 *N* ammonium thiocyanate. Each milliliter of 0.1 *N* ammonium thiocyanate is equivalent to 0.01003 g. of mercury or 0.01494 g. of methyl mercury dicyandiamide.

## PANOGEN 15 AND PANOGEN 42

See "Mercury," p. 1881, above.

## PARATHION OR METHYL PARATHION

## IN DUST AND WETTABLE POWDER FORMULATIONS

*Reagents* Ethyl Alcohol, 50%

Potassium Hydroxide, 1 *N* in 50% Alcohol

**Standard *p* Nitrophenol Solution**—Weigh 60 mg of *p* nitrophenol transfer to a 100 ml volumetric flask dissolve in the alcohol and make to volume Pipet 10 ml into a second 100 ml volumetric flask and make to volume Pipet 5 ml into a third 100 ml flask add 5 ml of 1 *N* potassium hydroxide and make to volume with the alcohol

**Procedure**—Weigh a sample containing about 10 mg of parathion and transfer to a 250 ml glass stoppered flask Add 100 ml of alcohol (50%) and shake periodically for 10 min Filter about 25 ml of this solution into a glass stoppered container

**Free *p* Nitrophenol**—Pipet 10 ml of the filtered solution into a 100 ml volumetric flask and dilute to volume with 50% alcohol Add 5 drops of 1 *N* potassium hydroxide mix and immediately measure the absorbance ( $A_n$ ) at 405 m $\mu$  Use 50% alcohol as the blank

**Parathion or Methyl Parathion**—Pipet 5 ml of the filtered solution into a 125 ml standard tapered flask add 5 ml of 1 *N* potassium hydroxide and add glass beads to prevent bumping Reflux for at least 30 min Cool and transfer to a 100 ml volumetric flask with 50% alcohol Dilute to volume with the alcohol and measure the absorbance ( $A$ ) at 405 m $\mu$  in 1 cm Corex cuvetts using 50% alcohol as the blank Determine the absorbance ( $A_s$ ) of the standard *p* nitrophenol solution in the same manner

Calculation —

$A$  = absorbance of sample solution,

$A_n$  = absorbance due to free *p* nitrophenol,

$A_s$  = absorbance of standard *p* nitrophenol solution,

$W$  = weight of sample, and

$W_s$  = weight of *p* nitrophenol standard  $0.060 \times \frac{100}{1000}$  (in 100 ml solution)

Factors Percentage of parathion  $\times 0.478$  = percentage of *p* nitrophenol

Percentage of methyl parathion  $\times 0.524$  = percentage of *p* nitrophenol.

$$\text{Percentage of free } p \text{ nitrophenol} = \frac{A_n W_s (100)}{A_s W \left( \frac{100}{1000} \right)}$$

$$\text{Percentage of (uncorrected) parathion} = \frac{A W_s (100)}{A_s W \left( \frac{100}{1000} \right) (478)}$$

$$\text{Percentage of parathion} = \text{percentage of (uncorrected) parathion} - \frac{1}{478} \\ (\text{percentage of free } p \text{ nitrophenol})$$

NOTE—The sample should contain about 10 mg of parathion (or methyl parathion) If necessary extract a larger sample and aliquot again before the determinations using alcohol as the solvent

## PERTHANE

See "Chlorine (Total)," p. 1860, and "Chlorine or Bromine in Organic Compounds," p. 1862, above.

PHENOTHIAZINE <sup>20</sup>

*Reagents.* Ethyl Alcohol, 95%.

Bromine Water, Saturated Solution.

**Standard Phenothiazine.**—Dissolve phenothiazine in 10 volumes of toluene with heating. For each 4 g. of phenothiazine, add 0.1 g. of carbon, reflux the mixture for 10 min., and filter it, while hot, through a heated filter. Cool the solution, collect the phenothiazine crystals with suction, and dry them in an oven at 100°C., and then in a vacuum desiccator containing paraffin chips. Repeat this recrystallization, if necessary, until the product melts at 184° to 185°C.

**Procedure.**—Weigh accurately a quantity of sample containing about 100 mg. of phenothiazine into a 500-ml. glass-stoppered bottle. Add exactly 200 ml. of ethyl alcohol, stopper the bottle, and shake it until the phenothiazine is completely dissolved. Transfer exactly 5 ml. of the clear, supernatant solution into a 100-ml. volumetric flask. Add 45 ml. of ethyl alcohol, and heat the mixture for 10 min. in a water bath at 60°C. Add rapidly, from a graduated cylinder, 5 ml. of bromine water, stopper the flask tightly, and allow it to stand for 10 min. at room temperature. Add an additional 5 ml. of bromine water, stopper the flask tightly, and allow it to stand for 10 min. at room temperature. Return the opened flask to the water bath, heat the bath to about 90°C., and continue heating for 5 min. after the alcohol vapors begin to escape from the flask. Cool the flask to room temperature, and dilute to volume with ethyl alcohol. The transmittancy is then determined at 520 m $\mu$ , using a blank sample to set the instrument.

A standard calibration curve is prepared from purified phenothiazine, using the exact analytical procedures as are used for the samples.

## PHORATE

See "Phosphorus (Organic)," following.

PHOSPHORUS (ORGANIC) <sup>21</sup>

This procedure may be used for phosphorus-containing organic compounds, including demeton, Dimefox, EPN, Isopestox, malathion, methyl parathion, 4-methylumbelliferone O,O-diethyl thiophosphate, para-oxon, parathion, schradan, sulfotepp, and tetraethyl pyrophosphate.

*Reagents.* Nitric Acid, Concentrated.

Potassium Chlorate.

Hydrochloric Acid, Concentrated.

Ammonium Molybdate, 2.5% Solution.

<sup>20</sup> Reproduced with permission from Analysis of Insecticides and Acaracides, Interscience Publishers, Inc., New York, 1955.

<sup>21</sup> Reproduced with permission from Analysis of Insecticides and Acaracides, Interscience Publishers, Inc., New York, 1955.



**Potassium Iodide Solution**—Dissolve 20 g of potassium iodide and 0.5 g of sodium carbonate in 80 ml of distilled water

**Sodium Sulfite, 0.5% Solution**

**Procedure**—An aliquot of a benzene solution containing about 0.1 mg of an organic phosphate compound is transferred to a 50 ml beaker, and the solvent is removed at room temperature by passing air over the surface of the solution. If the compound has a very high vapor pressure the evaporation should be done with extreme care, preferably with some cooling of the beaker. Introduce 2 ml of concentrated nitric acid into the beaker, cover it with a watch glass, and heat it on a hot plate for 5 min, then allow it to cool to room temperature. Add 0.10 g of potassium chlorate, swirl to dissolve the salt, and digest the mixture in the covered beaker on the hot plate for 15 to 20 min. Rinse down the cover glass and sides of the beaker with a minimum amount of water, and carefully evaporate just to dryness on the hot plate. If organic matter remains, avoid overheating which will cause charring.

Allow to cool slightly, add 2 ml of concentrated hydrochloric acid, rotate the beaker to insure that all the residue has been wetted, and again evaporate just to dryness as before. Repeat the addition of hydrochloric acid and evaporation to dryness twice more, washing down the sides of the beaker with the acid as it is added.

Dissolve the residue in 2 ml of distilled water and 1 ml of 10 N sulfuric acid solution, cover and boil the solution for 5 min. Cool, rinse down the cover with a minimum of water, and transfer the solution quantitatively to a 10 ml volumetric flask. Wash the beaker twice with 2 ml portions of water and add the washings to the volumetric flask. Cool to room temperature, add 1 ml of 2.5% ammonium molybdate solution, and then 1 ml of the potassium iodide sodium carbonate solution. Immerse the flask in a steam bath for 15 to 20 min. Cool to room temperature and add 0.5% sodium sulfite solution dropwise with frequent agitation until the iodine color disappears. Allow to stand for 15 to 20 min, and add more sulfite solution, in a similar manner if the iodine color reappears. Finally add 0.4 ml of 0.5% sodium sulfite solution, adjust to volume with water, and mix thoroughly. Determine the transmittancy at 650 m $\mu$  using a blank sample to set the instrument.

A standard calibration curve is prepared from the purified insecticide using the exact cleanup and analytical procedures as are used for the samples.

## PHOSPHORUS PASTES

### TOTAL PHOSPHORUS

**Reagents.** **Ammonium Molybdate Solution**—Dissolve 100 g of molybdic acid in dilute ammonium hydroxide (144 ml of strong ammonium hydroxide and 271 ml of water), and pour this solution slowly and with constant stirring into dilute nitric acid (489 ml of strong nitric acid and 1148 ml of water). Keep the mixture in a warm place for several days or until a portion heated to 40°C deposits no yellow precipitate of ammonium phosphomolybdate. Decant the solution from any sediment, and preserve in glass stoppered vessels.

**Ammonium Nitrate Solution**—Dissolve 100 g of commercial ammonium nitrate, free from phosphates in water, and dilute to 1 liter.

## PIVAL

**SPECTROPHOTOMETRIC DETERMINATION IN PRODUCTS  
CONTAINING ABOUT 0.025% PIVAL  
(2 PIVALYL 1,3-INDANDIONE)**

**Reagents** Sodium Pyrophosphate 1%—Dissolve 5 g of  $\text{Na}_4\text{P}_2\text{O}_7 \cdot 10\text{H}_2\text{O}$  in 500 ml of water

**Petroleum Ether**—Extract 200 ml of petroleum ether 3 times with 20 ml portions of 1% sodium pyrophosphate

**Procedure**—Weigh 10 g of sample into a Soxhlet thimble and extract with ethyl ether for about 4 hr. Transfer the extract to a 200 ml volumetric flask and make to the mark with ether. Pipet 3 ml into a glass stoppered test tube containing 10 ml of 1% sodium pyrophosphate stopper and shake vigorously for 2 min. Centrifuge at high speed until the aqueous layer is clear. Draw off the ether layer by means of an aspirator connected to a tube drawn out to a fine tip. Add about 2 ml of ether shake vigorously centrifuge and completely draw off the ether layer. Repeat with a second 2 ml of ether and then extract twice with petroleum ether in the same manner.

Prepare a blank solution by the same procedure using 2 ml of ether in place of the 2 ml of ether extract.

Determine the absorbance of the sodium pyrophosphate solution at 283  $m\mu$  in a 1 cm quartz cuvet.

Calculation—Percentage of pival =  $A(0.61)$

**NOTE**—Pival has maxima at 283, 312 and 321  $m\mu$  which may be used for identification.

**SPECTROPHOTOMETRIC METHOD FOR PRODUCTS  
CONTAINING ABOUT 0.5% PIVAL IN CORNSTARCH**

**Reagents** Ethyl Ether

Sodium Pyrophosphate Solution (1%)—Dissolve 5 g of  $\text{Na}_4\text{P}_2\text{O}_7 \cdot 10\text{H}_2\text{O}$  in 500 ml of water

**Petroleum Ether**—Extract 200 ml of petroleum ether 3 times with 20 ml portions of 1% sodium pyrophosphate solution

**Procedure**—Weigh 10 g of sample into a 125 ml glass stoppered flask and add 50 ml of ethyl ether with a pipet. Shake on a shaking machine for 30 min. Transfer about 15 ml to a glass stoppered test tube (6 in. by  $\frac{3}{4}$  in.) and centrifuge 5 min. at high speed or until the solution is clear. Take precautions to avoid evaporation of the ether.

(The centrifuging may be omitted if the diluent settles readily to give a clear solution.)

Pipet 10 ml of the clear ether extract into a 50 ml volumetric flask and dilute to the mark with ether.

Pipet 2 ml of this solution into a glass stoppered test tube containing exactly 10 ml of 1% sodium pyrophosphate solution and shake vigorously for 2 min. Centrifuge and draw off the ether layer by means of an aspirator connected to a tube drawn out to a fine tip. Add about 2 ml of ether shake vigorously centrifuge and draw off the ether layer. Repeat using 2 ml of petroleum ether in the same manner.

Prepare a blank solution in the same manner using 2 ml. of ether in place of the 2 ml. of ether extract.

Pipet a sufficient quantity (about 3 ml.) of the aqueous solution into a 1-cm., silica cuvet, and determine the optical density at 283  $m\mu$ .

Calculation.—Percentage of pival = optical density  $\times$  1.148.

NOTE.—Pival has maxima at 283, 312, and 324  $m\mu$ , which may be used for identification.

## PIVAL IN BAIT MATERIALS

### SPECTROPHOTOMETRIC DETERMINATION IN PRODUCTS CONTAINING ABOUT 0.025% PIVAL (2-PIVALYL-1,3-INDANDIONE)

*Reagents.* Sodium Pyrophosphate Solution (1%).—Dissolve 5 g. of  $\text{Na}_4\text{P}_2\text{O}_7 \cdot 10\text{H}_2\text{O}$  in 500 ml. of water.

Ethyl Ether-*n*-Hexane (20 to 80).—Extract 200 ml. of *n*-hexane 3 times with 20-ml. portions of 1% sodium pyrophosphate, and add 50 ml. of ethyl ether.

Hydrochloric Acid (1 + 4).

*Procedure.*—Weigh 2 g. of ground sample into a 125-ml., glass-stoppered flask, and add 50 ml. of 1% sodium pyrophosphate solution with a pipet. Shake for 1 to 2 hr. on a shaking machine. Transfer about 15 ml. to a glass-stoppered test tube, and centrifuge for at least 5 min. Pipet 10 ml. into a centrifuge tube, add 3 ml. of HCl (1 + 4) and 25 ml. of ether-hexane solution, and shake for 10 min. Centrifuge if necessary. Pipet 5 ml. of the solvent layer into a glass-stoppered test tube, and add 5 ml. of 1% sodium pyrophosphate. Prepare a blank by the same procedure, using the ether-hexane in place of the solvent layer. Shake for 2 min., centrifuge, and remove the solvent layer with an aspirator.

Determine the absorbance (*A*) of the sodium pyrophosphate solution at 283  $m\mu$  in a 1-cm., quartz cuvet.

A blank should be run on the bait material if it is available, and absorbance due to the bait should be subtracted from the absorbance obtained for the sample.

Calculation.—Percentage of pival =  $A(.057)$ .

NOTE.—Pival has maxima at 283, 312, and 324  $m\mu$ , which may be used for identification.

## PIVALYN (SODIUM SALT OF 2-PIVALYL-1,3-INDANDIONE)

### SPECTROPHOTOMETRIC DETERMINATION IN WATER-SOLUBLE POWDERS

#### METHOD 1

*Reagent.* Sodium Pyrophosphate, 2%.—Dissolve 10 g. of  $\text{Na}_4\text{P}_2\text{O}_7 \cdot 10\text{H}_2\text{O}$  in 500 ml. of water.

*Procedure.*—Prepare an aqueous solution of the sample containing 3 to 5  $\mu\text{g}$ . of Pivalyn per milliliter, and 1% sodium pyrophosphate.

For a product containing 0.14% Pivalyn, weigh 0.8 g. into a 100-ml. volumetric flask, dissolve in water, and make to volume. Pipet 15 ml. of this solution into a 50-ml. volumetric flask, add 25 ml. of 2% sodium pyrophosphate solution, and make to volume with water.

factor from the precipitated hydrazodicarbamide ( $\text{NH}_2\text{CONHNHCONH}_2$ ) to potassium cyanate is 0.68682.

### POTASSIUM CYANIDE

See "Sodium and Potassium Cyanides," p. 1903, below.

### PYRETHRUM POWDER<sup>22</sup>

#### PYRETHRIN I

**Reagents.** Denigés Reagent.—Mix 5 g. of yellow mercuric oxide with 40 ml. of water, and, while stirring, slowly add 20 ml. of sulfuric acid; then add an additional 40 ml. of water, and stir until completely dissolved. Test for the absence of mercurous mercury by adding a few drops of iodine monochloride solution to 10 ml., and titrating with standard potassium iodate solution, as instructed in the following procedure for determination, beginning with "Add 30 ml. of hydrochloric acid. . .".

**Iodine Monochloride Solution.**—Dissolve 10 g. of potassium iodide and 6.44 g. of potassium iodate in 75 ml. of water, in a glass-stoppered bottle. Add 75 ml. of hydrochloric acid and 5 ml. of chloroform, and adjust to faint iodine color (in chloroform) by adding dilute potassium iodide or potassium iodate solution. If much iodine is liberated, use a stronger solution of potassium iodate than 0.01 *M* at first, making final adjustment with an 0.01 *M* solution. Keep in the dark and readjust when necessary.

**Standard Potassium Iodate Solution, 0.01 *M*.**—Dissolve 2.14 g. of pure potassium iodate, previously dried at 105°C., in water, and dilute to 1 liter (1 ml. of this solution equals 0.0057 g. of pyrethrin I, and requires no further standardization).

**Procedure.**—Extract a sample containing 20 to 75 mg. of pyrethrin I (12.5 to 15 g.) in a Soxhlet or other efficient extraction apparatus for 7 hr., with petroleum ether. After extraction is complete, evaporate the petroleum ether to about 40 ml., stopper the flask, and place it in a refrigerator at 0° to 5°C. for at least 2 hr. or preferably overnight. Filter the cold extract through a cotton plug, saturated with cold petroleum ether, in the stem of a funnel, and collect the filtrate in a 250-ml. Erlenmeyer flask. Add 20 ml. of cold petroleum ether to the extraction flask. With a rubber policeman, dislodge resinous material in the flask, swirl the contents without allowing wash liquid to warm up appreciably, and filter through the cotton. Repeat the operation twice, using 10-ml. portions of the chilled petroleum ether. Add several glass beads, and remove the solvent on a water bath, without attempting to heat the residue long enough to remove the last traces of solvent.

Add 15 to 20 ml. of 0.5 *N* alcoholic sodium hydroxide to the flask containing the pyrethrum extract, connect to a reflux condenser, and boil gently for 1 to 1½ hr. Transfer to a 600-ml. beaker, and add sufficient water to bring the volume to 200 ml. Add a few glass beads, or preferably use a boiling tube, and boil down to 150 ml. Transfer to a 250-ml. volumetric flask and add 1 g. of Filter-Cel and 10 ml. of 10% barium chloride solution. Do not shake before diluting to volume. Dilute to volume, mix thoroughly, filter off 200 ml., neutralize with sulfuric acid (1 + 4),

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using 1 drop of phenolphthalein, and add 1 ml in excess (If necessary to hold the solution overnight at this point leave in alkaline condition) Filter through a 7 cm paper coated lightly with a suspension of Filter Cel in water, on a Buchner funnel, and wash several times with water. Transfer to a 500 ml separatory funnel and extract with two 50 ml portions of petroleum ether. Wash the extracts with two or three 10 ml portions of water and filter petroleum ether extract through a cotton plug into a clean 250 ml separatory funnel. Wash the cotton with 5 ml of petroleum ether. Extract the petroleum ether with 5 ml of 0.1 N sodium hydroxide, shaking vigorously. Drain the aqueous layer into a 100 ml beaker, wash petroleum ether with 5 ml of water or with an additional 5 ml of 0.1 N sodium hydroxide and add this to the beaker. Add 10 ml of the Deniges reagent and let stand 1 hr at  $25 \pm 2^\circ\text{C}$ . Add 20 ml of alcohol and precipitate mercurous chloride with 3 ml of saturated sodium chloride solution. Warm to about  $60^\circ\text{C}$  and filter through a small paper, transferring all the precipitate to the paper and wash with 10 ml or more of hot alcohol. Wash with 2 or more 10 ml portions of hot chloroform and place the paper and its contents in a 250 ml glass stoppered Erlenmeyer flask. Add 30 ml of hydrochloric acid and 20 ml of water and cool. Add 6 ml of chloroform or carbon tetrachloride and 1 ml of the iodine mono chloride solution and titrate with the potassium iodate solution shaking vigorously after each addition until no iodine color remains in the chloroform or carbon tetrachloride layer. Take as the end point the point at which the red color disappears from the chloroform or carbon tetrachloride layer. From the volume of the standard potassium iodate solution used calculate the percent of pyrethrin I.

## PYRETHRIN II

**Procedure**—Use aqueous residue from the petroleum ether extraction in the pyrethrin I determination and filter through a Gooch crucible if necessary. Concentrate the filtrate to about 50 ml, and transfer it to a 500 ml separatory funnel. Acidify with 10 ml of hydrochloric acid and saturate with sodium chloride (acidified aqueous layer must be saturated with sodium chloride throughout the following extractions). Extract with 50 ml of ether drain the aqueous layer into a second separatory funnel, and extract again with 50 ml of ether. Continue extracting and draining the aqueous layer using 35 ml for the third and fourth extractions. Combine the 4 ether extracts, drain, and wash with three 10 ml portions of saturated sodium chloride solution. Filter the ether extracts through a cotton plug into a 500 ml Erlenmeyer flask, and wash the cotton with an additional 10 ml of ether. Evaporate the ether on a water bath, and remove any fumes of hydrochloric acid with a current of air and continued heating. Dry 10 min at  $100^\circ\text{C}$ . Add 2 ml of neutral alcohol and 20 ml of water, and heat to dissolve acid. Cool, filter through a Gooch crucible, if necessary, add 1 or 2 drops of phenolphthalein, and titrate with 0.02 N sodium hydroxide (1 ml is equal to 0.00371 g of pyrethrin II).

## PYRETHRUM EXTRACTS IN MINERAL OIL

### PYRETHRIN I

**Reagents**—See method for pyrethrum powder, above

**Procedure**—In the case of extracts and concentrates containing more than 200 mg per 100 ml of pyrethrins, dilute to that concentration with petroleum ether

to detect the presence of oxidized pyrethrins, indicated by the development of cloudiness in the diluted solution. If the solution is clear, proceed as below. If the solution is not clear, dilute the portion taken for analysis in the same manner, add 1 g. of Filter-Cel, place in a refrigerator for at least 2 hr., filter through a Gooch crucible, and wash with cold petroleum ether. Use the filtrate and washings for the determination.

Weigh or measure a quantity of sample that will contain 20 to 75 mg. of pyrethrin I, and transfer to a 300-ml. Erlenmeyer flask. Evaporate the petroleum ether, if necessary, on a water bath, without attempting to heat the residue long enough to remove the last traces of solvent. Add 20 ml. of normal alcoholic sodium hydroxide, or more if necessary, to the flask, connect to a reflux condenser, and boil gently for 1 to 1½ hr. Transfer to a 600-ml. beaker, and add sufficient water to make the aqueous layer 200 ml. If more than 20 ml. of alcoholic sodium hydroxide solution have been used, add enough water so that all alcohol will be removed when the volume has been reduced to 150 ml. Add a few glass beads, or preferably use a boiling tube, and boil the aqueous layer down to 150 ml. Transfer the contents of the beaker to a 500-ml. separatory funnel, and drain the aqueous layer into a 250-ml. volumetric flask. Wash the oil layer once with water, and add the washing to the aqueous portion. If a slight emulsion still persists after draining the aqueous layer and washings, add 2 to 3 ml. of 10% barium chloride solution, but do not shake vigorously after this addition, since reversed emulsions, difficult to separate, may form. To the aqueous solution in the 250-ml. volumetric flask, add 1 g. of Filter-Cel and 10 ml. or more of the barium chloride solution. Do not shake before diluting to volume. Dilute to volume, mix thoroughly, and filter off 200 ml. Test filtrate with barium chloride to see if sufficient has been added to obtain a clear solution. Neutralize with sulfuric acid (1 + 4), using 1 drop of phenolphthalein, and add 1 ml. in excess. Then proceed as in the method for pyrethrin I in pyrethrum powders above, beginning "Filter through a 7-cm. paper . . ."

NOTE.—Chrysanthemum monocarboxylic acid reacts with the Denigés reagent to form a series of colors beginning with phenolphthalein red, which gradually changes to purple, then to blue, and finally to bluish green. The color reaction is very distinct with 5 mg. of the acid, and quantities as low as 1 mg. can usually be detected. Therefore, no pyrethrin I should be reported if the color reaction is negative.

With samples containing much perfume or other saponifiable ingredients, it may be necessary to use as much as 50 ml. of normal alcoholic sodium hydroxide. When lethanes are present, after washing mercurous chloride precipitate with alcohol and chloroform, wash once more with alcohol and then several times with hot water.

## ROTENONE

### IN DERRIS AND CUBÉ POWDER

**Reagents.** Purified Rotenone.—Dissolve rotenone, with decolorizing carbon, in hot carbon tetrachloride, cool in an ice bath until precipitation of the rotenone-carbon tetrachloride solvate has ceased, filter on a Büchner funnel, and wash twice with ice-cold carbon tetrachloride. Concentrate the filtrate, crystallize, and filter as before. Transfer the crystals to a beaker, add about twice their volume of alcohol, and heat nearly to boiling. Cool to room temperature, filter in a Büchner funnel, drawing air through until most of the alcohol is removed. Dry the rotenone in air, then heat for 1 hr. at 105°C. (Mother liquors may be concentrated and the

solvent allowed to crystallize for further purification preparation of wash solutions or for seeding to induce crystallization in the analytical procedure)

**Rotenone Carbon Tetrachloride Solvent**—Precipitate rotenone from a carbon tetrachloride solution filter by suction and dry in air

**Ethyl Alcohol**—Saturated with rotenone at room temperature

**Decolorizing Carbon** Norit A or equal

**Procedure**—Weigh 30 g (if the sample contains more than 7% rotenone use a quantity that will give 10 to 15 g of rotenone in a 200 ml aliquot) of finely powdered root and 10 g of decolorizing carbon into a 500 ml glass stoppered Erlenmeyer flask. Add 300 ml of chloroform measured at a definite room temperature place the flask on a shaking machine and agitate vigorously for at least 4 hr (preferably overnight). Keep stopper securely fastened. Filter the mixture rapidly into a suitable flask using a fluted paper without suction and keeping the funnel covered with a watch glass to avoid loss from evaporation. Stopper the flask and adjust the temperature of the filtrate to that of the original chloroform.

Transfer exactly 200 ml of the solution to a 500 ml Erlenmeyer flask and distill until only about 35 ml remain. Evaporate almost to dryness on a steam bath or a current of air. Remove the remainder of the solvent under reduced pressure heating cautiously on a steam bath when necessary. Use a vent in the stopper to avoid excessive vacuum. Dissolve the extract in 15 ml of hot carbon tetrachloride and again in a similar manner remove all of the solvent. Repeat with another 10 to 15 ml portion of hot carbon tetrachloride. This treatment removes all of the chloroform from the resins. The chloroform extract is usually completely soluble in carbon tetrachloride. If small amounts of insoluble material remain the purification procedure described below will eliminate them.

Dissolve the residue in about 10 ml of hot carbon tetrachloride and transfer to a 50 ml Erlenmeyer flask that has been marked to indicate a 25 ml volume. Rinse the 500 ml flask with hot carbon tetrachloride to remove the last traces of extract adding the wash solution to the carbon tetrachloride solution in the 50-ml flask. If the volume of solution at this point exceeds or is less than 25 ml adjust to 25 ml by evaporation on a steam bath or by addition of carbon tetrachloride. Cool the flask in an ice bath for several minutes stopper the flask and swirl until crystallization is apparent. Seed with a few crystals of rotenone carbon tetrachloride solvent if necessary to induce crystallization. If at this stage only a small quantity of crystalline material separates add an accurately weighed quantity of purified rotenone estimated to be sufficient to assure that the final result expressed as pure rotenone is at least 1 g. Then warm to effect a complete solution and again induce crystallization. At the same time prepare a saturated solution of rotenone in carbon tetrachloride for washing. Place the flasks containing the extract and wash solution in an ice bath capable of maintaining a temperature of 0°C and allow to remain overnight. After 17 to 18 hr in the ice bath rapidly filter the extract through a weighed Gooch crucible fitted with a disc of filter paper removing the flask from the ice bath only long enough to pour each fraction of extract into the crucible. Rinse the residue of crystalline material from the flask and wash under suction once with ice cold saturated rotenone carbon tetrachloride wash solution. Not more than 12 to 15 ml of wash solution should be used for rinsing and washing and the wash solution should be kept as near 0°C as possible during use. Allow the crucible to remain under suction about 5 min then dry to constant weight at 40°C (about 1 hr). The weight obtained is crude rotenone carbon tetrachloride solvent.

Break up the contents of the crucible with a spatula, mix thoroughly, and weigh 1 g. into a 50-ml. Erlenmeyer flask. Add 10 ml. of the alcohol that has been saturated with rotenone at room temperature, and swirl flask for a few minutes, stopper tightly, and set aside at least 4 hr., preferably overnight, at the same temperature. Filter on a weighed Gooch crucible fitted with a disc of filter paper. Rinse the crystals from the flask, and wash under suction with the alcohol saturated with rotenone at the temperature of crystallization (about 10 ml. is usually required). Allow the crucible to remain under suction 3 to 5 min., and dry at 105°C. to constant weight (about 1 hr.).

Multiply the weight of the residue by the weight of the total crude rotenone-carbon tetrachloride solvate, and to the product add 0.07 g. (0.07 g. represents the correction for the rotenone held in solution in the 25 ml. of carbon tetrachloride used for crystallization). If any pure rotenone has been added, subtract its weight from the value obtained. This gives the weight of pure rotenone contained in the aliquot of the extract.

The most important precaution in using this method is to keep the temperature of the carbon tetrachloride-rotenone wash solution and crucibles as near 0°C. as possible.

## ROTENONE

### IN DERRIS AND CUBÉ POWDER IN PRESENCE OF SULFUR

*Procedure.*—Follow the preceding method for rotenone to the point of adding decolorizing carbon to the solution. Use not more than 5 g. of carbon, and follow the procedure until the 200-ml. aliquot is evaporated to dryness on a steam bath. Add 10 ml. of acetone to the residue, warm to dissolve the rotenone, cool in running tap water or ice water for 15 min., filter through a disc of filter paper in a Gooch crucible, and wash 2 or 3 times with small portions of cold acetone (5- or 10-ml. each). Transfer the acetone solution to a 125-ml. Erlenmeyer flask, and evaporate almost to dryness on a steam bath in a current of air. Then completely remove the remainder of the solvent under reduced pressure, heating cautiously on the steam bath, when necessary to hasten the evaporation. If the residue appears to contain sulfur, repeat the extraction with acetone, using a smaller quantity of the reagent.

From this point proceed as directed above in the rotenone method, beginning "Dissolve the residue in about 10 ml. of hot carbon tetrachloride . . ."

## SABADILLA <sup>23</sup>

*Procedure.*—Weigh 10 g. of mixed 50% sabadilla dust (or a corresponding quantity of lesser concentration) into a 500-ml., glass-stoppered Erlenmeyer flask. Add exactly 300 ml. of ether-chloroform (3:1), and shake 5 min. Make alkaline with 10 ml. of ammonium hydroxide and shake for 2 hr. on a shaking machine. Let stand overnight; then shake 1 hr.

Filter, avoiding evaporation. Place a 200-ml. aliquot in a 500-ml. separatory funnel, acidify with sulfuric acid (3:97), and shake. Withdraw a small amount of the aqueous layer and test with litmus paper, returning the solution to the funnel.

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Add 50 ml of the dilute sulfuric acid and shake. Let separate and transfer acid extract to a second 500 ml separatory funnel. Add 50 ml of petroleum ether to the acid extract and shake. Let the layers separate and transfer the acid extract to a third funnel. Repeat the extraction of the solution in the first funnel with two 50 ml portions of the dilute sulfuric acid using the same 50 ml of petroleum ether in the second funnel for washing. Collect the acid extracts in the third separatory funnel.

Make acid extracts alkaline to phenolphthalein with ammonium hydroxide. Extract with three 50 ml portions of chloroform. Wash each chloroform extract by shaking gently with the same 100 ml portion of water in a fourth separatory funnel. If in emulsion form, add a small amount of anhydrous sodium sulfate.

Filter each chloroform extract through cotton into a weighed 250 ml flask. Evaporate the chloroform on a steam bath. Add a few milliliters of alcohol and evaporate again. Dry for 1 hr at 100 C. and weigh the sabadilla alkaloids.

### SCHRADAN

See Phosphorus (Organic) p 1891 above

### SEVIN

#### INFRARED DETERMINATION

**Standard Solution** Weigh 80 mg of pure Sevin (1 naphthyl N-methylcarbamate) into a 10 ml volumetric flask and make to volume with chloroform ACS grade.

**Procedure**—For dusts containing at least 10% Sevin weigh a sample containing 0.4 g of Sevin into a glass stoppered Erlenmeyer flask, add 50 ml of chloroform with a pipet stopper and shake for 20 min on a shaking machine. Centrifuge a portion of the extract to clarify.

For dusts containing less than 10% of Sevin weigh a sample containing 0.2 g of Sevin into a chromatographic tube (about 25 mm in diameter and 25 cm long) to which 3 g of Hyflo Supercel has been added, tamp gently and extract with 2 successive 50 ml portions of acetone, allowing the acetone to percolate through the sample. Collect the extract in a flask. Evaporate the solvent completely on a steam bath using an air current. Dissolve the residue in chloroform, transfer to a 25 ml volumetric flask and make to volume.

Transfer the sample solution to a sodium chloride cell and scan using the following settings for a Perkin Elmer model 21 infrared spectrophotometer:

Cell	0.5 mm, compensated with chloroform
Range	8.5 to 9.5 $\mu$
Resolution	960 (program)
Speed	2
Gain	adjusted (about 5)

Repeat with the standard solution. Measure the absorbance of the Sevin peak at 8.94  $\mu$  using a baseline from 8.8 to 9.3  $\mu$  and calculate the percentage of Sevin.

#### ULTRAVIOLET DETERMINATION

**Standard Solution**—Dissolve 100 mg of Sevin in 100 ml of ethyl alcohol. Pipet 2 ml into a 100 ml volumetric flask and make to volume with alcohol (100 ml 2 mg).

**Procedure.**—Prepare an extract containing about 2 mg. of Sevin in 100 ml. of ethyl alcohol. Extract by shaking for 30 min. in a 250-ml. Erlenmeyer flask with 100 ml. of alcohol.

Transfer the sample solution and the standard solution to 1-cm., silica cuvetts, and determine the absorbance at 280  $m\mu$  with alcohol as a blank, using a suitable spectrophotometer.

Calculate the percentage of Sevin as follows:

$$\text{Sevin, per cent} = \frac{A(.100)(\frac{2}{100})(100)}{A_s(1)(\frac{5}{50})} = \frac{2A}{A_s}$$

where  $A$  = absorbance of sample solution, and

$A_s$  = absorbance of standard solution.

NOTE.— $A_s$  = about 0.612. Sevin has a secondary maximum at 271  $m\mu$ . Sevin is rapidly decomposed in alkaline solution.

## SODIUM CHLORATE

### DETERMINATION IN HERBICIDES

**Reagents.** Potassium Permanganate.—Standard 0.1  $N$  solution.

Ferrous Sulfate Solution.—Thirty g.  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ , 900 ml. water, sulfuric acid to make 1 liter.

Manganese Sulfate Solution (Zimmermann Reinhart Solution).—Seventy g.  $\text{MnSO}_4 \cdot 4\text{H}_2\text{O}$ , 125 ml. sulfuric acid, 125 ml. 85% phosphoric acid diluted to 1 liter.

**Procedure.**—Shake 30 g. of sample with exactly 250 ml. of water in a glass-stoppered flask for 2 hr. Filter, transfer a 25-ml. aliquot to a 300-ml. Erlenmeyer flask, add exactly 30 ml. of ferrous sulfate solution, and boil for 10 min. The flask should be fitted with a Bunsen valve to prevent oxidation by the air. Cool, dilute to 100 ml., add 10 ml. of the manganese sulfate solution, and titrate with the potassium permanganate to the first distinct pink color, adding the solution dropwise toward the end. The end point is not permanent due to oxidation of the chloride by the permanganate. Standardize the ferrous sulfate solution by the same procedure. The difference between the volumes of permanganate solution used for the ferrous sulfate and for the sample is equivalent to the sodium chlorate (1 ml. 0.1  $N$   $\text{KMnO}_4$  = 0.001774 g.  $\text{NaClO}_3$ ).

## SODIUM AND POTASSIUM CYANIDES

### CYANIDE

**Reagent.** Silver Nitrate Solution, 0.1  $N$ .—Standardized accurately by appropriate method.

**Procedure.**—Break the sample into small lumps in a mortar (do not grind). Weigh quickly about 5 g. into a weighing bottle, and wash into a 500-ml. volumetric flask containing about 200 ml. of water. Add a little lead carbonate to precipitate any sulfides that may be present, dilute to the mark with water, mix thoroughly, and filter through a dry filter. Transfer a 50-ml. aliquot to a 400-ml. beaker, add 200 ml. of water, 5 ml. of sodium hydroxide solution (100 g. per liter of water), and 10 drops of saturated potassium iodide solution (or a few crystals), and titrate to faint opalescence with the silver nitrate solution. In making this titration it is advantageous to have the beaker over a black surface. From the amount of silver

nitrate solution used calculate the percentage of cyanide (1 ml of 0.1 N silver nitrate is equal to 0.005204 g of cyanide)

### SODIUM DIMETHYLDITHIOCARBAMATE <sup>24</sup>

The method given for Ferbam may be used the only difference being in the factor used in calculation Calculate the percentage of sodium dimethyldithiocarbamate as follows

$$\text{NaDMDTC per cent} = \frac{(A - B) \times N \times 14.3215}{\text{sample weight (grams)}}$$

where *A* = milliliters of 0.1 N iodine in determination titration,

*B* = milliliters of 0.1 N iodine in blank titration, and

*C* = normality of 0.1 N iodine

### SODIUM FLUOSILICATE

See Fluorine Present as Sodium Fluosilicate p 1878 above

### SULFENONE

See Chlorine (Total) p 1860 and Chlorine or Bromine in Organic Compounds p 1862 above

### SULFOTEPP

See Phosphorus (Organic) p 1891 above

### TDE

See Chlorine (Total) p 1860 and Chlorine and Bromine in Organic Compounds p 1862 above

### TETRAETHYL PYROPHOSPHATE <sup>25</sup>

*Apparatus* Weighing Buret (5 to 10 ml Capacity)

Cylindrical Funnel—Approximately 1 in diameter by 3 in long packed with 1 in of cotton

*pH Meter (Optional)*

*Reagents* Acetone, 25% Solution in Water—Five hundred ml of acetone ACS grade are mixed with 1500 ml of water and cooled to 25°C

Sodium Hydroxide, 0.1 N

Hydrochloric Acid, 0.1 N

Indicator Aqueous solution 0.1% of methyl red or chlorophenol red

Amberlite IR-4B Resin—Analytical grade (from Resinous Products and Chemical Company Philadelphia Pa)

<sup>24</sup> Furnished by the Methods Clearing House Committee of the Association of American Pesticide Control Officials Inc

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**Preparation and Use of Resin Column.**—Weigh 30 g. of amberlite resin which has been previously screened to remove all particles under 30-mesh, slurry with water, and pour into a 100-ml. buret containing a small plug of glass wool at the bottom. Wash the resin column with 150 ml. of 3% aqueous sodium hydroxide solution at a flow rate of approximately 5 ml. per min., and then rinse with water at a flow rate of about 25 ml. per min. until the effluent is colorless to phenolphthalein. Displace the water by washing with 25% aqueous acetone solution. Do not allow the column to run dry, or channeling may result. Maintain the liquid level at all times approximately 1 in. above the resin bed.

Expand the resin bed after each determination, and before introducing a new sample, because the resin tends to pack in the column as it absorbs acidic material. Accomplish this renovation simply by back-washing with 25% aqueous acetone, introduced by means of a large funnel and rubber hose at the base of the column until the liquid level reaches the top of the buret. After the resin settles, drain off to the customary height of 1 in. above the resin bed. The next sample may now be received in the column.

After 8 to 10 samples have been passed through the column, it will be necessary to remove the adsorbed acidic material. Accomplish the regeneration of the resin by repeating the initial treatment with 3% aqueous sodium hydroxide, water, and 25% acetone solution as described above.

It is important before introducing a sample, to test the effluent from the column. If yellow, the column should be washed with 25% aqueous acetone until it is *entirely colorless*.

**Procedure.** (I) For Purified or Technical Grades of Tetraethyl Pyrophosphate Not Mixed With a Solvent, Emulsifying Agent, Etc.—Transfer from a weighing buret, taking precautions to exclude atmospheric moisture, a 2.5-g. sample (1.0-g., if the tetraethyl pyrophosphate content is over 50%), weighed to the nearest milligram by difference, to 50 ml. of 25% aqueous acetone contained in a 125-ml. separatory funnel. Mix the sample with the acetone solution by swirling, and allow it to stand 15 min. at  $25^{\circ} \pm 2^{\circ}\text{C}$ . Run the sample solution through the column by gravity at a rate of approximately 25 ml. per min. Wash the column and funnel with three 50-ml. portions of 25% aqueous acetone, added successively, and maintain a 2.5-cm. liquid level above the resin at all times.

Catch the combined effluent in a 250-ml. volumetric flask, dilute to volume with water, mix, and transfer a 100-ml. aliquot to a 250-ml. beaker. Add 50 ml. of 0.1 *N* sodium hydroxide, stir well, and allow to stand at room temperature for 30 min.; then back-titrate with 0.1 *N* hydrochloric acid to a pH of 6.0, using a pH meter. Methyl red or chlorophenol red may be used as an indicator if a pH meter is not available. Calculate the percentage of tetraethyl pyrophosphate by use of the following formula:

$$\frac{\text{Net milliliters of } 0.1 \text{ } N \text{ NaOH} \times 0.0145 \times 1.016 \times 2.5 \times 100}{\text{weight of sample}} = \text{percentage of tetraethyl pyrophosphate,}$$

$$\frac{\text{or net milliliters of } 0.1 \text{ } N \text{ NaOH} \times 3.67}{\text{weight of sample}} = \text{percentage of tetraethyl pyrophosphate.}$$

(II) For Formulations of Tetraethyl Pyrophosphate Containing an Organic Solvent With or Without an Emulsifying Agent.—Transfer from a weighing buret, taking precautions to exclude atmospheric moisture, a 2.5-g. sample, weighed to

the nearest milligram by difference to 50 ml of 25% aqueous acetone solution by swirling. If an oil tends to separate out continue the swirling occasionally during 15 min at  $25 \pm 2^\circ\text{C}$ . Run the sample through a cylindrical funnel packed with 1 in. of cotton to absorb the oil and thence through the resin column at a rate of approximately 25 ml per min catching the effluent in a 250 ml volumetric flask. Wash the separatory funnel, the cylindrical funnel containing the cotton and the resin column with 3 successive 50 ml portions of 25% aqueous acetone. Maintain at all times a 2.5 cm liquid level above the resin. Proceed from this point as directed in procedure (1) beginning. Catch the combined effluent in a 250 ml volumetric flask.

### TETRAMETHYLTHIURAM DISULFIDE (THIRAM M)<sup>26</sup>

**Reagents and Apparatus** Standard Sodium Sulfide Solution 0.0333 M (approximately)—Prepare by dissolving 8 g of c.p.  $\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$  in 292 ml of distilled water and filtering into 700 ml of c.p. methyl alcohol. Sparge the reagent solution for 30 min with nitrogen using a suitable fritted glass diffuser and bubbling the nitrogen through the first 2 scrubber solutions of the dispensing system (see Fig. 39.5). Store the reagent solution in the reservoir of the automatic leveling buret maintaining a slight nitrogen pressure in the dispensing system.

**Thiram M, Recrystallized**—Recrystallize the commercial product at least twice from a mixture of chloroform and methyl alcohol.

**Acetone**—c.i. or technical grade.

**Nitrogen Atmosphere Dispensing System** This should consist of a mercury U tube gas washing bottle containing silver salt scrubber solution, gas washing bottle containing sodium sulfide reagent solution, nitrogen and water reservoir and an automatic leveling buret 50 ml capacity. For assembly and identification of the apparatus see Fig. 39.5.

**Silver Salt Scrubbing Solution**—Prepare this solution as follows: dissolve 4 g of 2-anthraquinonesulfonic acid sodium salt (Eastman #700) in 200 ml of hot distilled water, cool and add 32 g of sodium hydrosulfite reagent grade, stir to dissolve and add 13.2 g of sodium hydroxide pellets. This solution volume is capable of removing oxygen from about 250 l of nitrogen. The solution is exhausted when its color changes from blood red to brown. At this point remove from the line and add fresh solution.

**Nitrogen Gas**—A cylinder supply with necessary pressure reducing valve. Instructions are attached for manipulation of the dispensing system. **Caution**—Carefully regulate the nitrogen pressure ahead of the needle valve so that it does not exceed 10 lbs.

**pH Meter**—Such as Beckman Laboratory AC Model H 2 with No. 700 adapter. Use Beckman No. 43462 sleeve type calomel electrode.

**Procedure** Standardization (See NOTE 1 below) (1) Accurately weigh 0.30 to 0.50 g of recrystallized Thiram M and transfer to a clean and dry 400 ml beaker. (2) Add 200 ml of acetone and swirl for several minutes to dissolve the Thiram which dissolves slowly at room temperature. (3) Titrate with the sodium sulfide standard solution using the pH meter and determine the end point by the differential method (second derivative equal to zero at the end point see NOTE 2). Note

<sup>26</sup> Furnished by the Methods Clearing House Committee of the Association of American Pesticide Control Officials, Inc.

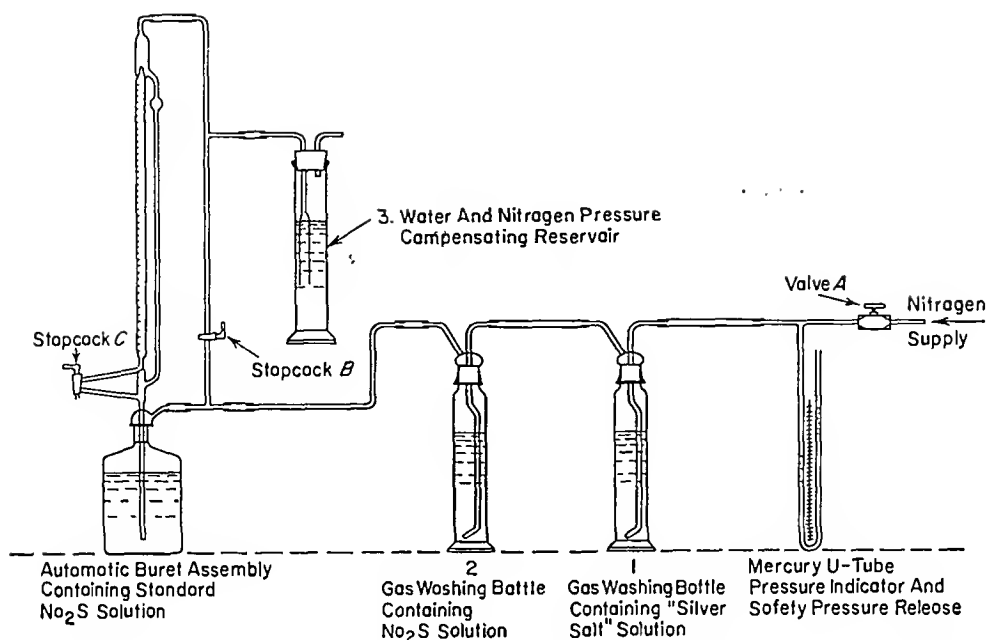


FIG. 39-5. Apparatus for Nitrogen Blanketing and Dispensing of Sodium Sulfide Solution.

the mv. reading at this point. (4) From the milliliters of sodium sulfide standard solution required to reach the stoichiometric point, calculate the solution factor, grams of active ingredient per milliliter of solution, by:

$$\frac{\text{weight of purified Thiram M}}{\text{milliliters of sodium sulfide reagent}}$$

$$= \text{grams of tetramethylthiuram disulfide per milliliter}$$

**Determination.**—(1) Accurately weigh 0.30 to 0.35 g. of sample, and proceed exactly as in steps (1) to (3) in the standardization, above. (2) From the milliliters of standard sodium sulfide solution required and the solution factor, calculate the percentage of tetramethylthiuram disulfide by:

$$\frac{\text{milliliters of sodium sulfide solution} \times \text{factor} \times 100}{\text{weight of sample}} = \text{tetramethylthiuram disulfide}$$

**NOTE 1.**—The sodium sulfide standard solution, when blanketed with nitrogen, should be standardized each day determinations are made. Data have been obtained that indicate that a daily change in the solution factor is significant enough to necessitate this daily standardization.

**NOTE 2.**—For routine analyses made immediately following, and under the same conditions as, the standardization titration, the titrations of the unknowns may be carried to the same mv. reading without significant error. For the highest accuracy, however, and for interlaboratory cross-checks the differential method for end point detection should be used.

**Manipulation of the Sodium Sulfide System.**—(1) *Filling the Buret.*

to boiling, add 50 ml. of 10% potassium iodide solution, stir, and let stand overnight. Filter through a tight Gooch crucible containing 2 discs of S&S 589 white ribbon paper, covered by a medium pad of asbestos. Wash 4 or 5 times with 10-ml. portions of 1% potassium iodide solution, and finally with absolute alcohol. Dry to constant weight at 105°C. (1 to 1½ hr.), and weight as thallous iodide. From this weight calculate the percentage of thallium as thallous sulfate, using a factor of 0.7619.

## THIODAN <sup>29</sup>

### DETERMINATION IN TECHNICAL THIODAN AND FORMULATIONS

*Reagents.* Standard Iodine Solution, 0.1 N.

Standard Sodium Thiosulfate Solution, 0.1 N.

*Procedure.*—Weigh out a sample of product large enough to contain 0.4 to 0.6 g. of Thiodan, and place in an 8-oz., screw-cap bottle or glass-stoppered flask. (Liquid formulations and technical Thiodan may be placed directly into 100 ml. of methanol for the hydrolysis step below.)

Add 100 ml. methanol by pipet (hexane should be used for extraction when highly colored extracts are obtained).

Shake for 15 min. by hand or on a reciprocating type shaker, 1 in. stroke, approximately 280 cycles per min., and filter into a 100-ml. graduated cylinder.

Transfer a 50-ml. aliquot by means of a pipet (with methanol extraction, proceed directly with hydrolysis step). Transfer hexane extracts into a 250- or 500-ml. Erlenmeyer flask, and remove the hexane by evaporation to near dryness, by placing the flask on a hot water bath in a hood.

Add 100 ml. of distilled methanol, 15 pellets of sodium hydroxide, and reflux gently for 2 hr.

Wash down the condenser with 20 ml. of methanol, and add 50 ml. of distilled water. Add 1 drop of 1% phenolphthalein, and neutralize with (1 + 4) sulfuric acid. Add a few drops of dilute sodium hydroxide to restore the indicator color and prevent loss of sulfur dioxide.

For the accurate determination of sulfite, it is necessary to add the sodium sulfite to an excess of acidified standard iodine solution and back-titrate the excess of iodine with thiosulfate.

To a 500-ml. iodine flask, add approximately 35 ml. of standard 0.1 N iodine solution from a buret. Add 1 ml. of (1 + 4) sulfuric acid. While agitating on a magnetic stirrer, slowly pour in the sulfite solution. Rinse the flask well with small portions of distilled water until all sulfite has been transferred. (The washing procedure should be continued until there is insufficient sulfite in the flask to bleach a small drop of iodine.) The final volume in the iodine flask should be 225 to 250 ml.

Back-titrate the excess iodine with 0.1 N thiosulfate, using 10 ml. of 0.2% starch solution as the indicator, and titrating to the disappearance of the blue color.

Compare the iodine and thiosulfate solutions by titrating about 40 ml. of iodine solution added to 175 ml. of water and acidified with 1 ml. of (1 + 4) sulfuric acid with thiosulfate, to the same starch end point used in the determination. This should be done each day analyses are made. Use the ratio to calculate the milli-

<sup>29</sup> Furnished by the Methods Clearing House Committee of the Association of American Pesticide Control Officials, Inc.

liters of iodine solution equivalent to the milliliters of thiosulfate consumed in the back titration, and subtract this to obtain the milliliters of iodine consumed by the Thiodan

**Calculation.**—

$$\frac{\text{milliliters of 0.1000 N iodine} \times 2.035}{\text{grams sample}} = \text{percentage of thiodan}$$

## THIODAN

### TOTAL CHLORINE METHOD

See Chlorine (Total) p 1860 and Chlorine and Bromine in Organic Compounds, p 1862, above

## THIRAM

### DETERMINATION BY ULTRAVIOLET SPECTROPHOTOMETRY

**Reagents** Thiram (Tetramethylthiuram Disulfide)—Melting point 148°C. May be purified by recrystallization from chloroform ethyl alcohol

**Standard Solution**—Thiram 10 µg per milliliter in chloroform. Transfer 100 mg thiram to a 100 ml volumetric flask, make to volume with chloroform, quantitatively dilute 5 ml to 50 ml, and dilute 5 ml of this solution to 50 ml

**Procedure**—Prepare a chloroform solution of the sample, aliquoting if necessary, containing about 10 µg per milliliter of thiram. Determine the absorbance at 280 mµ of the sample and standard solutions with chloroform as the blank, using a spectrophotometer and 1 cm silica cells. Calculate the percentage of thiram from the absorbances for the sample and the standard. The absorbance for a solution containing 10 µg of thiram per milliliter is about 0.505.

The absorbance curve for the sample may be determined to aid in the identification of thiram. The absorbance from 285 mµ to 260 mµ is nearly constant with a slight maximum at 280 mµ. Other substances, such as ziram, which absorb at 280 mµ, interfere.

## TOXAPHENE

See Chlorine (Total), p 1860, and Chlorine or Bromine in Organic Compounds, p 1862, above

## TRITHION

See Phosphorus (Organic), p 1891, above

## WARFARIN

This method is applicable for most bait materials, including pellet form baits and specially coated grains containing about 0.025% warfarin.

**Reagents.** Sodium Pyrophosphate Solution.—Dissolve 5 g of  $\text{Na}_4\text{P}_2\text{O}_7 \cdot 10\text{H}_2\text{O}$  in 500 ml of water.



**Ethyl Ether-"Skellysolve B" Mixture.**—Extract 200 ml. of "Skellysolve B" 3 times with 20-ml. portions of 1% sodium pyrophosphate solution, and prepare a 20 to 80 mixture of ethyl ether and the treated "Skellysolve B."

**Hydrochloric Acid Solution, 2.5 N.**

**Procedure.**—Weigh 2 g. of finely ground sample into a 125-ml., glass-stoppered flask, and add 50 ml. of 1% sodium pyrophosphate solution. Shake for 1 hr. on a mechanical shaker. Transfer 30 to 35 ml. to a glass-stoppered centrifuge tube, and centrifuge for at least 5 min. Pipet 25 ml. into a second centrifuge tube, add 5 ml. of 2.5 N HCl, followed by 50 ml. of ethyl ether-"Skellysolve B" mixture, and shake 5 min. If an emulsion forms, centrifuge for a few minutes. Pipet 20 ml. of the ether layer into another centrifuge tube, and add 10 ml. of 1% sodium pyrophosphate solution. Shake for 2 min., and remove the ether layer. If the aqueous phase is not clear, centrifuge for a few minutes with the stopper removed. Pipet a sufficient quantity (about 3 ml.) of the aqueous solution into a 1-cm., quartz cuvet, and determine its optical density at 308  $m\mu$  with a spectrophotometer, against 1% sodium pyrophosphate.

**Calculation.**—

$$\frac{\text{Optical density-blank}^{30}}{.459} \times 0.025 = \text{percentage of warfarin.}$$

## WARFARIN

### METHOD FOR PRODUCTS CONTAINING ABOUT 0.5% WARFARIN IN CORNSTARCH

**Reagents.** Ethylene Dichloride.

1% Sodium Hydroxide Solution (0.25 N).

**Procedure.**—Weigh a 0.6-g. sample into a 125-ml., glass-stoppered flask, and add 50 ml. of ethylene dichloride with a pipet. Shake on a shaking machine for at least 10 min. Transfer to a centrifuge tube, stopper, and centrifuge 5 min. at high speed, or until clear.

Pipet 2 ml. of the ethylene dichloride extract into a glass-stoppered cylinder, add 10 ml. of 1% NaOH solution with a pipet, and shake for 1 min. by hand. Prepare a blank solution in the same manner, using 2 ml. of ethylene dichloride in place of the extract.

Decant the sodium hydroxide layer into a centrifuge tube, and centrifuge until clear. Pipet a sufficient amount of the alkali layer (approximately 3 ml.) into a quartz cuvet (1-cm. cell), and determine the optical density at 308  $m\mu$ , using a spectrophotometer.

**Calculation.**—The optical density of a solution of 1 mg. of warfarin in 100 ml. of 1% sodium hydroxide was found to be 0.463, using the above procedure. If  $D$  is the optical density obtained,

$$\text{Percentage of warfarin} = \frac{D(\frac{1.0}{100})(100)}{(0.463)(1000)(.6)(\frac{2}{50})} = D(.9000)$$

<sup>30</sup> Whenever possible, the specific bait material in the sample without warfarin should be evaluated for the most accurate warfarin value.

## WARFARIN

## DETERMINATION OF SODIUM SALT (0.54%) IN MIXTURE WITH WHITE SAND

**Reagent** 2% Sodium Pyrophosphate Solution

**Procedure**—Weigh a 4.8 g sample into a 1000 ml volumetric flask add 500 ml of water shake to dissolve the sodium salt of warfarin make to volume with water and mix

Pipet 5 ml in a glass stoppered tube add 5 ml of 2% sodium pyrophosphate solution Prepare a blank solution of 5 ml of 2% sodium pyrophosphate solution and 5 ml of water

Pipet a sufficient quantity (about 3 ml) of the sodium pyrophosphate solution into a 1 cm quartz cuvet and determine the absorbance at 308 mμ using a spectrophotometer

**Calculation**—

$$\text{Percentage of warfarin} = \frac{A(\frac{100}{1000})(100)}{(0.463)1000(4.8)(1.000)} = A(9000)$$

$$\text{Percentage of Na salt} = \text{percentage of warfarin} \times 1.071$$

ZINEB<sup>31</sup>

(Parzate Zineb Fungicide)

The method given for Terbam may be used for Zineb the only difference being in the factor used in calculation Calculate the percentage of zinc ethylene bis dithiocarbamate as follows

$$\text{Percentage of zineb} = \frac{(A - B) \times N \times 13.787}{\text{sample weight (grams)}}$$

where  $A$  = milliliters of 0.1 N iodine in determination titration,

$B$  = milliliters of 0.1 N iodine in blank titration and

$N$  = normality of 0.1 N iodine

<sup>31</sup> Furnished by the Methods Clearing House Committee of the Association of American Pesticide Control Officials Inc

## Chapter 40

# PETROLEUM AND PETROLEUM PRODUCTS<sup>1</sup>

By Robert W. Chaffin and John D. Christena

Rock Island Refining Corp.  
Indianapolis, Ind.

### FLASH POINT BY TAG CLOSED TESTER<sup>2</sup>

This method describes a test procedure for determining the flash point of all mobile liquids flashing below 175°F. (79°C.). The method is intended to be applicable to lacquer solvents and diluents of low flash point, but not products classed as fuel oil.

**NOTE.**—For the determination of flash points of fuel oils, use ASTM Method D93, Test for Flash Point by Pensky-Martens Closed Tester, p. 1923.

**Outline of Method.**—The sample is placed in the cup of the tester and, with the lid closed, heated at a slow constant rate. A small flame of specified size is directed into the cup at regular intervals. The flash point is taken as the lowest temperature at which application of the test flame causes the vapor above the sample to ignite.

**Apparatus.** Tag Closed Tester.—The Tag closed tester should consist of the test cup, lid with test flame, and liquid bath conforming to the following requirements:

**Test Cup**, of brass or other nonrusting metal of equivalent heat conductivity and should conform to dimensional requirements prescribed in Table 40-1. It should weigh  $68 \pm 1$  g.

TABLE 40-1. DIMENSIONAL REQUIREMENTS

Depth of bath liquid surface below top of test cup.....	$1.094 \pm 0.016$ in.
Depth of sample surface below top of test cup.....	$1.156 \pm 0.031$ in.
Depth of bottom of bulb of test thermometer below top of cup when in place.....	$1.77 \pm 0.03$ in.
Inside diameter of test cup at top.....	$2.125 \pm 0.005$ in.
Diameter of bead on top of cover.....	$0.156 \pm 0.031$ in.
Diameter of opening in tip of test flame nozzle.....	$0.049 \pm 0.010$ in.
Outside diameter of tip of test flame nozzle.....	0.079 in. max.

<sup>1</sup> Most of the methods included in this chapter are Standards of the American Society for Testing and Materials, and are reproduced with permission.

<sup>2</sup> Standardized as ASTM D56-61, and ASA No.: Z11.24-1961.

**Lid**—The lid comprises a circle of nonrusting metal with a rim projecting downward about  $\frac{5}{16}$  in (1.59 cm) a slide shutter a device which simultaneously opens the shutter and depresses the tip of the tube which carries fuel through to the test flame and a slanting collar in which the cup thermometer ferrule is inserted. Figure 40.1 gives a diagram of the upper surface of the lid showing dimensions

and positions of the three holes opened and closed by the shutter and the size and position of the opening for the cup thermometer.

The rim should fit the collar of the liquid bath with a clearance not exceeding 0.002 in (0.05 mm) and should be slotted in such a manner as to press the lid firmly down on the top of the cup when the latter is in place in the bath. When this requirement is not met the vertical position of the cup in the bath should be suitably adjusted as by placing a thin ring of metal under the flange of the cup.

The shutter should be of such size and shape that it covers the three openings in the lid when in the closed position and uncovers them completely when in the open position. The nozzle of the flame exposure device should conform to the dimensions given in Table 40.1.

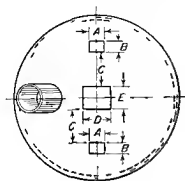
The device shall be designed and constructed so that opening the shutter depresses the tip to a point approximately 0.08 in (2 mm) to the right of the horizontal center of the middle opening of the lid. (Refer to Fig. 40.2.) This will bring the test flame to the approximate center of the opening. The plane of the underside of the lid should be between the top and bottom of the opening in the tip of the flame exposure device when the latter is fully depressed.

The collar for the cup thermometer ferrule should be set at an angle which permits placement of the thermometer with its bulb approximately in the horizontal center of the cup at a depth prescribed in Table 40.1.

**Liquid Bath**, conforming to the limiting or minimum dimensions shown in Fig. 40.2. It should be of brass, copper or other noncorroding metal of substantial construction. Sheet metal of about No. 20 B & S gage is satisfactory. It may if desired be lagged with heat insulating material to facilitate control of temperature.

**Heater** of any type (electric, gas, alcohol, etc.) capable of controlling temperature as required under Procedure (below). An external electric heater controlled by a variable voltage transformer is recommended.

**Bath Stand**—For electric heating any type of stand may be used. For alcohol lamp or gas burner a stand as illustrated in Fig. 40.3 to protect the flame from air currents (unless tests can be made in a draft free room) is required.



- A - 0.281  
B - 0.188  
C - 0.594  
D - 0.469  
E - 0.406

All Dimensions 0.005  
Unless Otherwise Shown

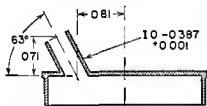


FIG. 40.1 Top of Lid Showing Position and Dimensions of Openings (Dimensions Relating to the Size and Position of the Thermometer Collar Are Recommended but Not Mandatory.)

Shield.—A shield 18 in. (46 cm.) square and 24 in. (61 cm.) high, open in front, is recommended.

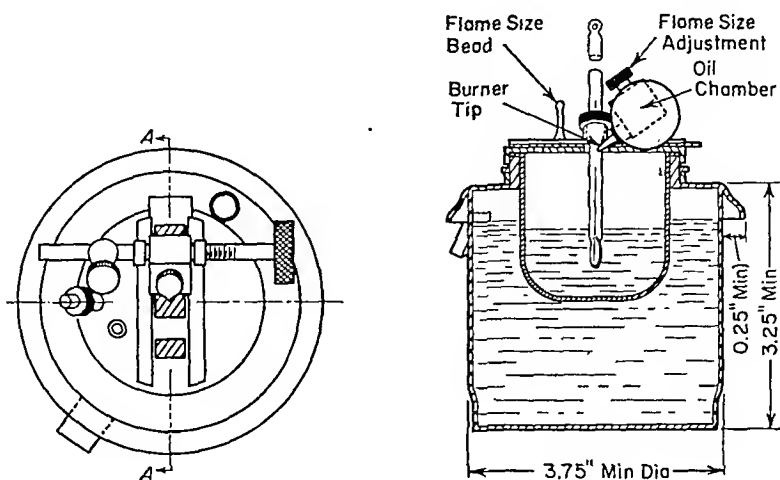


FIG. 40-2. Section of Liquid Bath and Cup.

**Thermometers.**—For the test cup thermometer, use one as prescribed in Table 40-2. For the bath thermometer, any convenient type which has an adequately open scale covering the required range may be used; it is often convenient to use the same type of thermometer as used in the test cup.

TABLE 40-2. THERMOMETERS

For Tests.....	Below 40°F. (4°C.)	At 40 to 120°F. (4 to 49°C.)	Above 120°F. (49°C.)
Use ASTM Thermometer <sup>a</sup> . . .	57F. or 57C.	9F. or 9C. 57F. or 57C.	9F or 9C.

<sup>a</sup> Complete specifications for these thermometers are given in ASTM Standard E 1-61.

**NOTE.**—Whenever thermometers complying with ASTM requirements are not available, thermometers complying with the requirements for The Institute of Petroleum thermometer IP 15F. P.M.-Low may be used.

**Checking Condition and Operation of Tag Closed Testers.** **Material.**—*p*-Xylene, conforming to the following requirements:

Specific gravity (60/60°F.) . . . . 0.860 minute. 0.866 max.

Boiling range . . . . 2°C. max. from start to dry point, when tested by ASTM Method D850, Test for Distillation of Industrial Aromatic Hydrocarbons, or Method D1078, Test for Distillation Range of Lacquer Solvents and Diluents. The range shall include the boiling point of pure *p*-xylene, which is 138.35°C.(281.03°F.).

Purity 95% minimum, calculated in accordance with ASTM Method D1016, Test for Determination of Purity from Freezing Points of High-Purity Compounds, from the experimentally determined freezing point, measured by ASTM Method D1015, Test for Measurement or Freezing Points of High-Purity Compounds for Evaluation of Purity

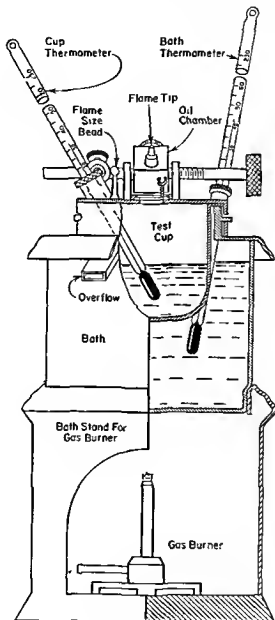


FIG. 403 Tag Closed Flash Tester

*Procedure*—Determine the flash point of the *p*-xylene, following the directions given below. When the tester is operating properly, a value of  $81 \pm 1^\circ\text{F}$  ( $27.2 \pm 0.6^\circ\text{C}$ ) will be obtained.

*Sample.*—Erroneously high flash points may be obtained if precautions are not taken to avoid the loss of volatile material. Containers shall not be opened unnecessarily and transfers shall not be made unless the sample temperature is at least 20°F. (11°C.) below the expected flash point. Samples in leaky containers shall be discarded.

*Preparation of Apparatus.*—Support the tester on a level steady table. Unless tests are made in a draft-free room or compartment, surround the tester on three sides by the shield for protection from drafts. Tests made in a laboratory draft hood or near ventilators are not to be relied upon.

Gas is recommended for the test flame. If gas is not available, insert a wick of cotton in the burner tip, place small quantity of cotton waste in the chamber to which the burner tip is attached, and fill the chamber with signal, sperm, or lard oil.

*Procedure.*—For flash points of 55°F. (13°C.) or higher, fill the bath with water until it starts to overflow. For lower flash points, use as the bath liquid a mixture of water and ethylene glycol (permanent-type radiator antifreeze) or any other suitable liquid of low viscosity and suitably low freezing point (NOTE). The temperature of the liquid in the bath shall be at least 20°F. (11°C.) below the expected flash point at the time of introduction of the sample into the test cup. Do not cool the bath liquid by direct contact with carbon dioxide or Dry Ice. Place the test cup in position in the bath.

NOTE.—Due to possible difficulty in maintaining the prescribed rate of temperature rise and due to the formation of ice on the lid, results by this method for samples having flash points below 32°F. (0°C.) may be somewhat unreliable. Trouble due to ice formation on the slide may be minimized by carefully lubricating the slide shutter with high-vacuum silicone lubricant.

Using a graduate and taking care to avoid wetting the cup above the final liquid level, measure  $50 \pm 0.5$  ml. of the sample into the cup, both the sample and graduate being precooled, if necessary, so that the sample temperature at the time of measurement will be  $60 \pm 10^\circ\text{F.}$  ( $16 \pm 5.6^\circ\text{C.}$ ) or at least 20°F. (11°C.) below the expected flash point, whichever is lower. It is essential that the sample temperature be maintained at least 20°F. (11°C.) below the expected flash point during the transfers from the sample container to the graduate and from the graduate to the test cup. Destroy air bubbles on the surface of the sample. Wipe the inside of the cover with a clean cloth or absorbent tissue paper; then attach the lid, with the thermometer in place, to the bath collar.

Light the test flame, adjusting it to the size of the small bead on the cover. Adjust the heat so that the temperature of the sample will rise at a rate of 1°F. (0.6°C.) per  $30 \pm 3$  seconds.

When the temperature of the sample in the test cup is 10°F. (5.6°C.) below its expected flash point, operate the mechanism on the cover in such a manner as to introduce the test flame into the vapor space of the cup, and immediately bring it up again. The time consumed for the full operation shall be about 1 second, or the time required to pronounce distinctly the words "thousand and one." Avoid any jerkiness in the operation of depressing and raising the test flame.

Repeat the application of the test flame after each 1°F. (0.6°C.) rise in temperature of the sample in the test cup, discontinuing the test and removing the source of heat when a distinct flash is observed in the interior of the cup. Do not confuse the true flash with the bluish halo which sometimes surrounds the test flame during

applications immediately preceding the actual flash. Record the temperature of the sample when the flash point is reached.

Lift the lid and wipe off the thermometer bulb. Remove the sample cup empty and wipe dry.

If at any time between the first introduction of the test flame and the observation of the flash point the rise in temperature of the sample is not within the range  $1^{\circ}\text{F}$  ( $0.6^{\circ}\text{C}$ ) per  $30 \pm 3$  seconds or if the actual flash point differs from the expected flash point by an amount greater than the applicable repeatability limit (see Precision below) discard the result and repeat the test adjusting the source of heat to secure the proper rate of temperature rise and/or using a modified expected flash point as required.

**NOTE**—Never make a repeat test on the same portion of sample once used; always take a fresh portion of sample for each test.

**Correction for Barometric Pressure**—Observe and record the barometric pressure at the time of the tests. When the pressure differs from 760 mm of mercury correct the flash point by means of the following equation, the corrected flash point being recorded to the nearest whole number:

$$\text{Corrected flash point} = F + 0.06(760 - P)$$

where  $F$  = observed flash point in degrees Fahrenheit and

$P$  = barometric pressure in millimeters of mercury

**Precision**—The following data should be used for judging the acceptability of results (90% probability):

Duplicate results by the same operator should be considered suspect if they differ by more than  $2^{\circ}\text{F}$  ( $1.1^{\circ}\text{C}$ ).

The result submitted by one laboratory should not be considered suspect unless it differs from that of another laboratory by more than the following amounts:

<i>Flash Point</i>	<i>Reproducibility</i>
Below $55^{\circ}\text{F}$ ( $12.8^{\circ}\text{C}$ )	$6^{\circ}\text{F}$ ( $3.3^{\circ}\text{C}$ )
$55^{\circ}\text{F}$ ( $12.8^{\circ}\text{C}$ ) or above	$4^{\circ}\text{F}$ ( $2.2^{\circ}\text{C}$ )

## FLASH AND FIRE POINTS BY CLEVELAND OPEN CUP<sup>3</sup>

This method describes a test procedure for determining the flash and fire points of all petroleum products except fuel oils and those having an open cup flash below  $170^{\circ}\text{F}$  ( $79^{\circ}\text{C}$ ).

**NOTE**—This method may occasionally be specified for the determination of the fire point of a fuel oil. For the determination of the flash points of fuel oils use ASTM Method D93, Test for Flash Point by Means of the Pensky Martens Closed Tester. ASTM Method D93 should also be used when it is desired to determine the possible presence of small but significant concentrations of lower flash point substances which may escape detection by Method D92. ASTM Method D1310, Test for Flash Point of Volatile Flammable Materials by Tag Open Cup Apparatus may be employed if the flash point is below  $170^{\circ}\text{F}$  ( $79^{\circ}\text{C}$ ) as determined by Method D92.

**Outline of Method**—The test cup is filled to a specified level with sample. The temperature of the sample is increased fairly rapidly at first and then at a slow

<sup>3</sup> Standardized as ASTM D92-57 and ASA No. Z11.6-1957.



constant rate as the flash point is approached. At specified intervals a small test flame is passed across the cup. The lowest temperature at which application of the test flame causes the vapors above the surface of the liquid to ignite is taken as the flash point. To determine the fire point, the test is continued until the application of the test flame causes the oil to ignite and burn for at least 5 seconds.

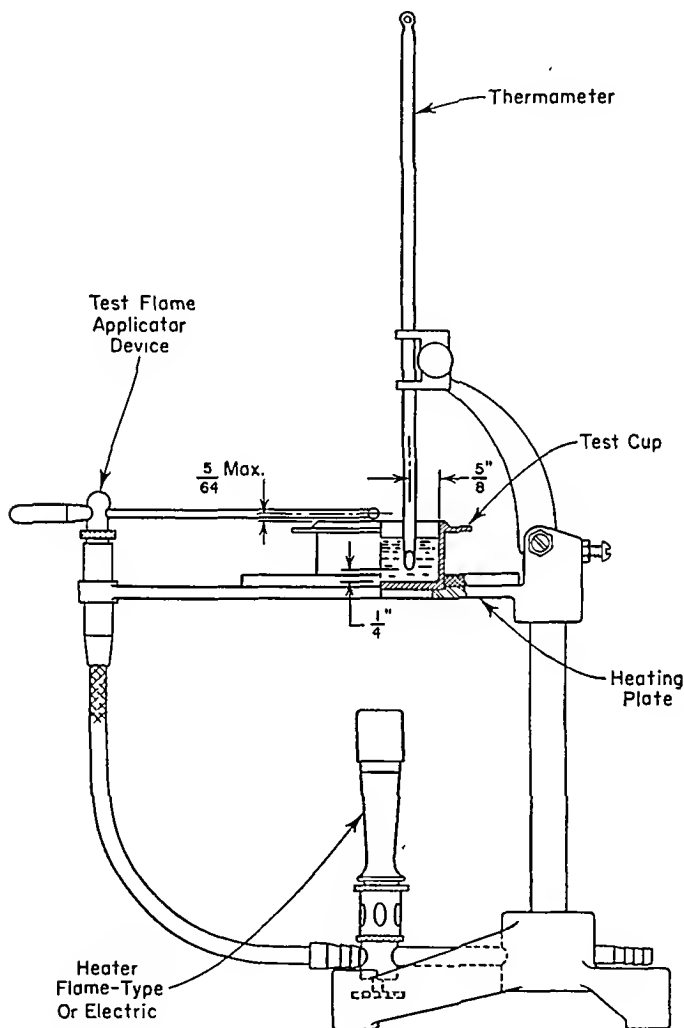


FIG. 40-4. Cleveland Open Cup.

**Apparatus.** Cleveland Open Tester.—The apparatus consists of the test cup, heating plate, test flame applicator, heater, and supports as described in detail below. The assembled apparatus and heating plate are illustrated in Figs. 40-4 and 40-5, respectively.

**Test Cup,** conforming to the dimensional requirements shown in Fig. 40-4 and Table 40-3. The cup may be equipped with a handle.

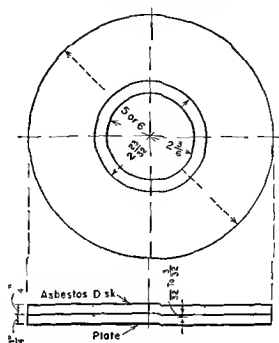


FIG. 405 Heating Plate

TABLE 403 DIMENSIONAL REQUIREMENTS FOR CLEVELAND OPEN FLASH CUP

	Inches		
	Min	Normal	Max
Inside diameter immediately below filling mark	$2\frac{1}{32}$	$2\frac{1}{2}$	$2\frac{1}{32}$
Outside diameter below flange	$2\frac{1}{8}$	$2\frac{1}{8}$	$2\frac{1}{2}$
Inside height from center of bottom to rim	$1\frac{9}{32}$	$1\frac{1}{8}$	$1\frac{1}{32}$
Thickness of bottom	$\frac{7}{64}$	$\frac{1}{8}$	$\frac{9}{64}$
Distance from rim to filling mark	$\frac{3}{8}$	$\frac{1}{2}$	$\frac{5}{8}$
Distance lower surface flange to bottom of cup	$1\frac{7}{8}$	$1\frac{1}{2}$	$1\frac{9}{8}$
Vertical distance upper surface flange to rim	$\frac{7}{64}$	$\frac{1}{8}$	$\frac{9}{64}$
Thickness of rim	$\frac{5}{64}$	$\frac{3}{32}$	$\frac{7}{64}$
Width of lower surface of flange	$\frac{9}{16}$	$1\frac{1}{8}$	$\frac{5}{8}$

*Heating Plate.*—A brass, cast iron, wrought iron, or steel plate with a center hole surrounded by an area of plane depression, and a sheet of hard asbestos board which covers the metal plate except over the area of plane depression in which the test cup is supported. The essential dimensions of the heating plate are shown in Fig. 40-5; however, it may be square instead of round, and the metal plate may have suitable extensions for mounting the test flame applicator device and the thermometer support. Also, a metal bead, as mentioned in the following paragraph, may be mounted on the plate so that it extends through and slightly above a suitable small hole in the asbestos board.

*Test Flame Applicator.*—The device for applying the flame may be of any suitable type, but it is suggested that the tip be approximately  $\frac{1}{16}$  in. (0.159 cm.) in diameter at the end, and that the orifice be  $\frac{1}{32}$  in. (0.08 cm.) in diameter. The device for operating the test flame may be mounted in such a manner as to permit automatic duplication of the sweep of the test flame, the radius of swing being not less than 6 in. (15 cm.) and the center of the orifice being supported so that it swings in a plane not greater than  $\frac{5}{64}$  in. (0.20 cm.) above the plane of the rim of the cup. It is desired that a bead, having a diameter of  $\frac{5}{32} \pm \frac{1}{32}$  in. ( $0.4 \pm 0.08$  cm.) be mounted in a convenient position on the apparatus so that the size of the test flame can be compared to it.

*Heater.*—Heat may be supplied from any convenient source. The use of a gas burner or alcohol lamp is permitted, but under no circumstances are products of combustion or free flame to be allowed to come up around the cup. An electric heater controlled by a variable voltage transformer is preferred. The source of heat shall be centered under the opening of the heating plate with no local superheating. Flame-type heaters may be protected from drafts or excessive radiation by any suitable type of shield that does not project above the level of the upper surface of the asbestos board.

*Thermometer Support.*—Any convenient device may be used which will hold the thermometer in the specified position during a test and which will permit easy removal of the thermometer from the test cup upon completion of a test.

*Heating Plate Support.*—Any convenient support which will hold the heating plate level and steady may be employed.

*Shield.*—A shield 18 in. (46 cm.) square and 24 in. (61 cm.) high, open front, is recommended but not required.

*Thermometer.*—An ASTM Open Flash Thermometer No. 11°F. (11°C.) having a range of 20 to 760°F. (−6 to +400°C.) and conforming to the requirements in ASTM Specifications E 1 is required.

NOTE.—Whenever thermometers complying with ASTM requirements are not available, thermometers complying with the requirements for The Institute of Petroleum thermometer IP 28F Cleveland may be used, provided that the scale error has been found to comply with ASTM requirements, or calibration corrections are used.

*Preparation of Apparatus.*—Support the tester on a level steady table in a draft-free room or compartment. Shield the top of the tester from strong light by any suitable means to permit ready detection of the flash point. Tests made in a laboratory hood (see Note) or any location where drafts occur are not to be relied upon. During the last 30°F. (17°C.) rise in temperature prior to the flash point, care must be taken to avoid disturbing the vapors in the test cup by careless movements or breathing near the cup.

Barometric pressure, mm. of mercury	Correction	
	deg. Fahr.	deg. Cent.
715 to 635	5	2.8
634 to 550	10	5.5

**Precision.**—The following data should be used for judging the acceptability of results (95% probability).

Duplicate results by the same operator should be considered suspect if they differ by more than the following amounts:

*Repeatability*

Flash point..... 15°F. (8.3°C.)  
Fire point..... 10°F. (5.5°C.)

The result submitted by one laboratory should not be considered suspect unless it differs from that of another laboratory by more than the following amounts:

*Reproducibility*

Flash point..... 30°F. (16.7°C.)  
Fire point..... 20°F. (11.1°C.)

## FLASH POINT BY PENSKY-MARTENS CLOSED TESTER <sup>4</sup>

This method of test describes a procedure for determining the flash point by Pensky-Martens closed tester of fuel oils as well as viscous materials and suspensions of solids, unless the use of another method is specified. This procedure is not applicable to drying oils, solvent-type liquid waxes, or cutback asphalts.

NOTE 1.—The flash point of cutback asphalts may be determined by Method D1310, Test for Flash Point of Volatile Flammable Materials by Tag Open-Cup Apparatus.

NOTE 2.—This method may be employed for the detection of contamination of lubricating oils by minor amounts of volatile material.

**Outline of Method.**—The sample is heated at a slow, constant rate with continual stirring. A small flame is directed into the cup at regular intervals with simultaneous interruption of stirring. The flash point is the lowest temperature at which application of the test flame causes the vapor above the sample to ignite.

**Apparatus.** ASTM Pensky-Martens Tester as described in Specifications E134, for Pensky-Martens Closed Flash Tester.

**Thermometers.**—Two standard thermometers should be used with the ASTM Pensky-Martens tester, as follows:

For tests in which the indicated reading falls within the limits 20° to 220°F., inclusive, an ASTM Pensky-Martens Low Range or Tag Closed Tester Thermometer

<sup>4</sup> Standardized as ASTM D93-61 and ASA No.: Z11.7-1958.

having a range of  $-5$  to  $+110^{\circ}\text{C}$  or  $20$  to  $230^{\circ}\text{F}$  and conforming to the requirements for thermometers 9C and 9F as prescribed in ASTM Specifications E1 should be used

For tests in which the indicated reading falls within the limits  $220$  to  $700^{\circ}\text{F}$  an ASTM Pensky Martens High Range Thermometer having a range of  $90$  to  $370^{\circ}\text{C}$  or  $200$  to  $700^{\circ}\text{F}$  and conforming to the requirements for thermometers 10C and 10F as prescribed in ASTM Specifications E1 should be used

The flash point as determined by means of thermometer 9F or 9C should govern with respect to establishing if thermometer 10F or 10C is to be employed

**NOTE**—Whenever thermometers complying with ASTM requirements are not available thermometers complying with the corresponding requirements of the Institute of Petroleum IP 15F (or 15C) PM—Low or IP 16F (or 16C) PM—High may be used Calibration corrections are to be used in temperature ranges where the IP requirements for scale accuracy are less stringent than those of ASTM

**Preparation of Apparatus**—Support the tester on a level, steady table Unless tests are made in a draft free room or compartment, it is good practice, but not required, to surround the tester on three sides with a shield, each section of which is about 18 in (46 cm) wide and 24 in (61 cm) high

**Preparation of Sample**—If the sample displays a haze or contains free water, bring it to a temperature at least  $30^{\circ}\text{F}$  ( $16^{\circ}\text{C}$ ) below its flash point and filter it through qualitative filter paper into a previously dried and cool container For viscous samples it may be preferable to filter the sample through a loose plug of absorbent cotton

The sample free of undissolved water, shall be brought to a temperature at least  $30^{\circ}\text{F}$  ( $16^{\circ}\text{C}$ ) below its expected flash point

**Procedure**—Thoroughly clean and dry all parts of the cup and its accessories before starting the test Take particular care to remove any gasoline or naphtha which had been used to clean the apparatus Fill the cup with the oil to be tested to the level indicated by the filling mark Place the lid on the cup and set the latter in the stove Take care to have the locking device properly engaged Insert the thermometer Light the test flame and adjust it to  $\frac{3}{8}$  in (4 mm) in diameter Supply heat at such a rate that the temperature as read on the thermometer increases  $9$  to  $11^{\circ}\text{F}$  ( $5$  to  $6^{\circ}\text{C}$ ) per minute Turn the stirrer  $90$  to  $120$  r p m, stirring in a downward direction

If the sample is known to have a flash point of  $220^{\circ}\text{F}$  or below, apply the test flame when the temperature of the sample reaches  $18^{\circ}\text{F}$  ( $10^{\circ}\text{C}$ ) below the expected flash point, and thereafter at each temperature reading that is a multiple of  $2^{\circ}\text{F}$  ( $1^{\circ}\text{C}$ ) The test flame is applied by operating the mechanism on the cover which controls the shutter and test flame burner so that the flame is lowered into the vapor space of the cup in  $0.5$  second left in its lowered position for  $1$  second and quickly raised to its high position Discontinue stirring while applying the test flame

If the sample is known to have a flash point above  $220^{\circ}\text{F}$ , apply the test flame in the manner just prescribed at each temperature that is a multiple of  $5^{\circ}\text{F}$  ( $2^{\circ}\text{C}$ ) beginning at a temperature of  $30^{\circ}\text{F}$  ( $16^{\circ}\text{C}$ ) below the expected flash point In order to maintain the test flame, it may be necessary to lower it into the vapor space of the cup in  $1$  second

Record as the flash point the temperature read on the thermometer at the time the test flame application causes a distinct flash in the interior of the cup Some

times the test flame during application is surrounded with a bluish halo as the flash point temperature is approached. Do not confuse the true flash with this halo.

### DETERMINATION OF FLASH POINT OF SUSPENSIONS OF SOLIDS

**Procedure.**—Bring the material to be tested and the tester to a temperature of  $60 \pm 10^\circ\text{F}$ . ( $15 \pm 5^\circ\text{C}$ .) or  $20^\circ\text{F}$ . ( $11^\circ\text{C}$ .) lower than the estimated flash point, whichever is lower. Completely fill the air space between the cup and the interior of the air bath with water at the temperature of the tester and sample. Turn the stirrer  $250 \pm 10$  r.p.m., stirring in a downward direction. Raise the temperature throughout the duration of the test at a rate of not less than  $2$  nor more than  $3^\circ\text{F}$ . ( $1$  to  $1.5^\circ\text{C}$ .) per min. With the exception of these requirements for rates of stirring and heating, proceed as prescribed in the preceding section.

**NOTE.**—Solid carbon dioxide ( $\text{CO}_2$ ) (Dry Ice) shall in no case be used to obtain the proper rate of temperature rise, since  $\text{CO}_2$  has a blanketing effect which leads to a false flash point.

**Barometric Pressure.**—Observe and record the barometric pressure. No correction shall be made except in case of dispute when the result shall be corrected on the following basis: for each inch (25 mm.) below 29.92 in. (760 mm.) barometric reading, add  $1.6^\circ\text{F}$ . ( $0.9^\circ\text{C}$ .) to the flash point; for each inch (25 mm.) above 29.92 in. (760 mm.) barometric reading, subtract  $1.6^\circ\text{F}$ . ( $0.9^\circ\text{C}$ .) from the flash point.

**Precision.**—The following data should be used for judging the acceptability of results (95% Probability):

**Repeatability.**—Duplicate results by the same operator should be considered suspect if they differ by more than the following amounts:

Material	Flash Point Range	Repeatability
Suspensions of solids.....	95 to $110^\circ\text{F}$ .	$4^\circ\text{F}$ .
All others.....	<div> <div>Below <math>220^\circ\text{F}</math>.</div> <div>Above <math>220^\circ\text{F}</math>.</div> </div>	<div> <div><math>4^\circ\text{F}</math>.</div> <div><math>20^\circ\text{F}</math>.</div> </div>

**Reproducibility.**—The results submitted by each of two laboratories should be considered suspect if they differ from each other by more than the following amounts:

Material	Flash Point Range	Reproducibility
Suspensions of solids.....	95 to $110^\circ\text{F}$ .	$6^\circ\text{F}$ .
All others.....	<div> <div>Below <math>220^\circ\text{F}</math>.</div> <div>Above <math>220^\circ\text{F}</math>.</div> </div>	<div> <div><math>6^\circ\text{F}</math>.</div> <div><math>25^\circ\text{F}</math>.</div> </div>

API GRAVITY OF PETROLEUM AND ITS PRODUCTS<sup>5</sup>

## HYDROMETER METHOD

This method describes a procedure for the determination by means of a glass hydrometer of the API gravity (in vacuum) of crude petroleum and of petroleum products normally handled as liquids and having a Reid vapor pressure of 26 lb or less. Results are determined at 60°F or converted to values at 60°F by means of standard Tables.

**NOTE**—The procedure for measurement of specific gravity 60/60°F by hydrometer is described in ASTM Method D1298. For measurement of specific gravity 77/77 for road oils, road tars, asphalt cements and soft tar pitches see ASTM Method D70. For measurement of specific gravity 77/77°F of hard penetration asphalt see ASTM Method D71. For measurement of specific gravity 15.56/15.56°C of industrial aromatics see ASTM Method D891. For measurement of density of hydrocarbon liquids see ASTM Method D941. For measurement of density and specific gravity of liquids by Bingham Pycnometer see ASTM Method D1217.

**Definition** API Gravity is defined by the following equation:

$$\text{API Gravity deg} = \frac{141.5}{\text{sp gr } 60/60^{\circ}\text{F}} - 131.5$$

**Apparatus**—The following apparatus is required:

**Hydrometers**, of glass graduated in degrees API (in vacuum) as listed in Table 40.4 and conforming to the Tentative Specifications for ASTM Hydrometers (ASTM

TABLE 40.4 AVAILABLE API HYDROMETERS

ASTM Designation	Type	API Range	
		Total	Each Hydrometer
1H to 10H	long plain form	-1 to 101	12
21H to 40H	short plain form	0 to 101	6
51H to 60H	thermo hydrometer	-1 to 101	12
71H to 74H	thermo-hydrometer	-1 to 41	12

Designation E100) For referee testing of petroleum products the long plain form of hydrometer (1H to 10H) should be used.

**Thermometers** having a range of -5 to +215°F and conforming to the requirements for Thermometer 12F as prescribed in ASTM Specifications E1.

**Hydrometer Cylinders**, made of metal, clear glass or plastic. For convenience in pouring the cylinder may have a lip on the rim. The inside diameter of the cylinder shall be at least 25 mm greater than the outside diameter of the hydrometer used in it. The height of the cylinder shall be such that the length of the

<sup>5</sup> Standardized as ASTM D287-55 and ASA No. Z11.31-1955.

column of sample it contains is greater by at least 25 mm. than the portion of the hydrometer which is immersed beneath the surface of the sample.

**Temperature of Test.**—The gravity determined by the hydrometer method is most accurate at or near the standard temperature of 60°F.; use this or any other temperature between 0 and 195°F. for test so far as it is consistent with the type of sample and necessary limiting conditions shown in Table 40-5.

TABLE 40-5. LIMITING CONDITIONS AND TEST TEMPERATURES

Sample Type	Gravity Limits	Initial Boiling Point Limits	Other Limits	Test Temperature
Highly volatile	Lighter than 70° API	—	—	Cool to 35°F. or lower in original closed container
Moderately volatile	Heavier than 70° API	Below 250°F.	—	Cool to 65°F. or lower in original closed container
Moderately volatile and viscous	Heavier than 70° API	Below 250°F.	Viscosity too high at 65°F.	Heat to minimum temperature for sufficient fluidity
Nonvolatile	Heavier than 70° API	Above 250°F.	—	Any temperature between 0 and 195°F. as convenient
Mixtures of non-petroleum with petroleum products	—	—	—	60 ± 0.25°F.

**Procedure.**—Adjust the temperature of the sample in accordance with Table 40-5. The hydrometer cylinder and thermometer shall be at approximately the same temperature as the sample to be tested.

Pour the sample into the clean hydrometer jar without splashing, so as to avoid the formation of air bubbles and to reduce to a minimum the evaporation of the lower-boiling constituents of the more volatile samples. For the more volatile samples, transfer to the hydrometer cylinder by siphoning. Remove any air bubbles formed, after they have collected on the surface of the sample, by touching them with a piece of clean filter paper before inserting the hydrometer. Place the cylinder containing the sample in a vertical position in a location free from air currents. Take precautions to prevent the temperature of the sample from changing appreciably during the time necessary to complete the test. During this period, the temperature of the surrounding medium should not change by more than 5°F.

Lower the hydrometer gently into the sample and, when it has settled, depress it about two scale divisions into the liquid and then release; keep the rest of the stem dry, as unnecessary liquid on the stem changes the effective weight of the instrument, and so affects the reading obtained. With samples of low viscosity, a slight spin imparted to the instrument on releasing assists in bringing it to rest, floating freely away from the walls of the hydrometer cylinder. Allow sufficient time for the hydrometer to become completely stationary and for all air bubbles to come to the surface. This is particularly necessary in the case of the more viscous samples.

When the hydrometer has come to rest, floating freely, and the temperature of the sample is constant to 0.2°F., read the hydrometer to the nearest scale division. The correct reading is that point on the hydrometer scale at which the surface of the liquid cuts the scale. Determine this point by placing the eye slightly below



the level of the liquid and slowly raising it until the surface, first seen as a distorted ellipse appears to become a straight line cutting the hydrometer scale

To make a reading with nontransparent oils observe the point on the hydrometer scale to which the sample rises above its main surface placing the eye slightly above the plane surface of the liquid This reading requires a correction Determine this correction for the particular hydrometer in use by observing the height above the main surface of the liquid to which the oil rises on the hydrometer scale when the hydrometer in question is immersed in a transparent oil having a surface tension similar to that of the sample under test

Observe the temperature of the sample to the nearest  $0.25^{\circ}\text{F}$  immediately before and after the observation of the gravity the liquid in the cylinder being thoroughly but cautiously stirred with the thermometer the whole of the mercury thread being immersed Should these temperature readings differ by more than  $1^{\circ}\text{F}$  repeat the temperature and gravity observations when the temperature of the sample has become more stable Record the mean of the thermometer reading before and after the final hydrometer reading to the nearest degree Fahrenheit as the temperature of the test

**NOTE**—When thermohydrometers are used stir the sample by carefully raising and lowering the hydrometer It is satisfactory in this case to read the thermometer scale after the hydrometer reading has been observed Because the thermometer incorporated in the hydrometer possesses certain inherent defects of design the precision of the reported value will be poorer than that described below

**Calculation**—When gravities have been observed on opaque liquids by the procedure given above subtract the correction in degrees API from the hydrometer reading observed

Correct all hydrometer readings to  $60^{\circ}\text{F}$  using Table 5 Reduction of Observed API Gravity to API Gravity at  $60^{\circ}\text{F}$  of the ASTM IP Petroleum Measurement Tables (American Edition)<sup>6</sup>

**NOTE**—The interconversion of API gravity to specific gravity is given in Table 3 API Gravity at  $60^{\circ}\text{F}$  to Specific Gravity at  $60^{\circ}\text{F}$  and to Density at  $15^{\circ}\text{C}$  of the ASTM IP Petroleum Measurement Tables (American Edition)<sup>6</sup>

Equivalent results can be obtained by determining specific gravity  $60/60^{\circ}\text{F}$  according to Method D1298 and converting the results to API Gravity at  $60^{\circ}\text{F}$  by means of Table 3 of the ASTM IP Petroleum Measurement Tables (American Edition)<sup>6</sup>

**Precision**—The following criteria should be used for judging the acceptability of results obtained at temperatures differing from  $60^{\circ}\text{F}$  by less than  $18^{\circ}\text{F}$

Degree API	Repeatability	Reproducibility
	Duplicate Results by the Same Operator	Average of Two Results in Each of Two Laboratories
	0.2	0.5

<sup>6</sup> Published jointly by and available from the American Society for Testing and Materials 1916 Race St Philadelphia 3 and the Institute of Petroleum 26 Portland Place London W 1 Companion volumes—the British Edition and the Metric Edition—are also available These tables supersede all other similar tables previously published by either of these Societies and the National Bureau of Standards Circular C-110 and the Supplement to Circular C-110

## DISTILLATION OF PETROLEUM PRODUCTS †

This method of test is intended for use in the distillation of motor gasolines, aviation gasolines, aviation turbine fuels, naphthas, kerosines, gas oils, distillate fuel oils, and similar petroleum products.

NOTE 1.—For the distillation of natural gasoline, see the Method of Test for Distillation of Natural Gasoline (ASTM Designation: D216).

NOTE 2.—For the distillation of aviation turbine fuels and other products of such wide boiling range that the low distillation thermometer specified in Group 3 of Table 40-6 is inadequate, this method may be applied by substituting the high distillation thermometer, together with the other test conditions specified in Group 3. (See section on Calculations and Reporting, p. 1937.)

**Definitions.** **Initial Boiling Point.**—The thermometer reading which is observed at the instant that the first drop of condensate falls from the lower end of the condenser tube.

**End Point.**—The maximum thermometer reading attained during the test, which usually occurs after the evaporation of all liquid from the bottom of the flask. The term "maximum temperature" is a frequently used synonym.

**Dry Point.**—The thermometer reading which is observed at the instant the last drop of liquid evaporates from the lowest point in the flask. Any drops or film of liquid on the side of the flask or on the thermometer are disregarded.

NOTE 3.—The end point, rather than the dry point, is intended for general use. The dry point may be reported in connection with special purpose naphthas, such as used in the paint industry. Also, it should be substituted for the end point whenever the sample is of such a nature that the precision of the end point cannot consistently meet the standard requirements now used.

**Decomposition Point.**—The thermometer reading which coincides with the first indications of thermal decomposition of the liquid in the flask.

NOTE.—Characteristic indications of thermal decomposition are an evolution of fumes, and erratic thermometer readings which usually show a decided decrease after any attempt is made to adjust the heat.

**Per Cent Recovered.**—The volume in milliliters of condensate observed in the receiving graduate, in connection with a simultaneous thermometer reading.

**Per Cent Recovery.**—The maximum per cent recovered, as observed in accordance with Procedure, p. 1936.

**Per Cent Total Recovery.**—The combined per cent recovery and residue in the flask, as observed in accordance with Procedure, p. 1936.

**Per Cent Loss.**—100 minus the per cent total recovery.

**Per Cent Residue.**The per cent total recovery minus the per cent recovery, or the volume of residue in milliliters if measured directly.

**Per Cent Evaporated.**—The sum of the per cent recovered and the per cent loss.

**Outline of Method.**—A 100-ml. sample is distilled under prescribed conditions which are appropriate to its nature (Table 40-7). Systematic observations of thermometer readings and volumes of condensate are made, and from these data, the results of the test are calculated and reported.

† Standardized as ASTM D86-61 and ASA No.: Z11.10-1961.

**Apparatus**—Typical assemblies of the apparatus are shown in Figs 40 6 and 40 7

**Distillation Flasks.**—Construction details and tolerances for flasks A and B are given in Fig 40 8

**Condenser and Cooling Bath.**—Typical approved types of condenser and cooling bath are included in Figs 40 6 and 40 7

TABLE 40-6 TEST CONDITIONS

	Group 1	Group 2	Group 3	Group 4
Sample characteristics				
Vapor pressure at 100°F lb (Reid Method ASTM D323 <sup>a</sup> )	9.5 or above	Below 9.5	Below 9.5	Below 9.5
Distillation { Initial Boiling Point <sup>b</sup> End Point <sup>b</sup>	— 482°F (250°C) or below	— 482°F (250°C) or below	212°F (100°C) or below Above 482°F (250°C)	Above 212°F (100°C) Above 482°F (250°C)
Preparation of apparatus				
Thermometer ASTM Distillation	Low 7F (7C)	Low 7F (7C)	Low 7F (7C)	High 8F (8C)
Diameter of Hole in Flask Support in	1 25	1 25	2 0	2 0
Temperature at start of test Flask and thermometer	55 to 65°F (13 to 18°C)	55 to 65°F (13 to 18°C)	55 to 65°F (13 to 18°C)	Not above ambient
Flask support and shield	Not above ambient	Not above ambient	Not above ambient	—
Graduate and 100-ml charge	55 to 65°F (13 to 18°C)	55 to 65°F (13 to 18°C)	55 to 65°F (13 to 18°C)	55°F (13°C) to ambient
Flask	A (100 ml)	A (100 ml)	B (125 ml)	B (125 ml)
Conditions during test procedure				
Temperature of condenser bath	32 to 34°F (0 to 1°C)	32 to 40°F (0 to 4°C)	32 to 40°F (0 to 4°C)	32 to 140°F* (0 to 60°C)
Temperature of bath around graduate	55 to 65°F (13 to 18°C)	55 to 65°F (13 to 18°C)	55 to 65°F (13 to 18°C)	Within ±5°F (±3°C) of temperature of distillation charge
Time from first application of heat to initial boiling point, minutes	5 to 10	5 to 10	5 to 10	5 to 15
Time from initial boiling point to 5 per cent recovered seconds	60 to 75	60 to 75	—	—
Uniform average rate of condensation from 5 per cent recovered to 5 ml residue in flask ml per minutes	4 to 5	4 to 5	4 to 5	4 to 5
Time from 5 ml residue to end point minutes	3 to 5	3 to 5	5 max	5 max

<sup>a</sup> Method of Test for Vapor Pressure of Petroleum Products (Reid Method) (ASTM Designation D323)

<sup>b</sup> As determined under all test conditions of the Group concerned

<sup>c</sup> The proper condenser bath temperature will depend upon the wax content of the sample and of its distillation fractions. The minimum temperature which permits satisfactory operation should be used. In general a bath temperature in the 32 to 40°F (0 to 4°C) range is suitable for kerosene and products meeting the specifications for Grade No. 1 fuel oil as prescribed in the Specifications for Fuel Oils (ASTM Designation D396) and those meeting the specifications for Grade No. 1 D diesel fuel oil as prescribed in the Classification of Diesel Fuel Oils (ASTM Designation D975). In some cases involving Grade No. 2 fuel oil (ASTM Specifications D396), Grade No. 2 D diesel fuel oil (ASTM Classification D975), gas oils and similar distillates it may be necessary to hold the condenser bath temperature at some point in the 100 to 140°F (38 to 60°C) range in order to avoid the condensation of solid waxy material in the condenser tube.

TABLE 40-7. VALUES OF THE CONSTANTS "A" AND "B" USED IN OBTAINING CORRECTED DISTILLATION LOSS

Observed Barometric Pressure, mm.	A	B
560	0.231	0.384
570	0.240	0.380
580	0.250	0.375
590	0.261	0.369
600	0.273	0.363
610	0.286	0.357
620	0.300	0.350
630	0.316	0.342
640	0.333	0.333
650	0.353	0.323
660	0.375	0.312
670	0.400	0.300
680	0.428	0.286
690	0.461	0.269
700	0.500	0.250
710	0.545	0.227
720	0.600	0.200
730	0.667	0.166
740	0.750	0.125
750	0.857	0.071
760	1.000	0.000

The condenser shall be made of seamless brass tubing, 22 in. (55.88 cm.) in length. It shall be  $\frac{3}{16}$  in. (14.29 mm.) in outside diameter, and shall have a wall thickness of 0.031 to 0.036 in.

The condenser shall be set so that approximately 15.5 in. (39.4 cm.) of the tube will be in contact with the cooling medium, with about 2 in. outside the cooling bath at the upper end, and about  $4\frac{1}{2}$  in. outside at the lower end. The length of tube projecting at the upper end shall be straight and shall be set at an angle of 75 deg. with the vertical. The section of the tube inside the cooling bath may be either straight or bent in any suitable continuous, smooth curve. The average gradient shall be 0.26 in. per linear inch of condenser tube (sine of angle of  $15^\circ$ ), and no section of the immersed portion of the condenser tube shall have a gradient less than 0.24 in. nor more than 0.28 in. per linear inch of tube. The projecting lower portion of the condenser tube shall be curved downward for a length of 3 in. (7.62 cm.) and slightly backward so as to insure contact with the wall of the receiving graduate at a point approximately 1 to  $1\frac{1}{4}$  in. (2.54 to 3.18 cm.) below the top of the graduate when it is in position to receive the distillate. The lower end

of the condenser tube shall be cut off at an acute angle so that the tip may be brought into contact with the wall of the cylinder

The capacity of the cooling bath shall be not less than 340 cu in (5.55 l) of cooling medium. The arrangement of the tube in the cooling bath shall be such that its center line shall be not less than  $1\frac{1}{4}$  in below the plane of the top of the bath at its point of entrance and not less than  $\frac{3}{4}$  in above the floor of the bath at its exit

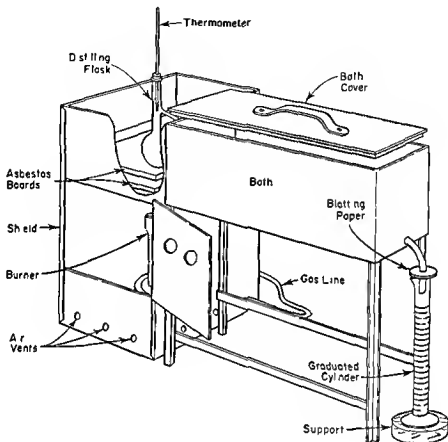


FIG 406 Apparatus Assembly Using Gas Burner

Clearances between the condenser tube and the walls of the bath shall be at least  $\frac{1}{2}$  in except for the sections adjacent to the points of entrance and exit. Multiple installations are permissible provided they conform to the dimensional requirements and the capacity of the bath is not less than 310 cu in per tube.

**Metal Shield or Enclosure for Flask.** *Type 1 Shield* (Fig 406) is 19 in high, 11 in long and 8 in wide made of sheet metal of approximately 22 gage. It shall have a door on one narrow side and two openings 1 in in diameter equally spaced in each of the two narrow sides with a slot cut in one side for the vapor tube. The centers of these four openings shall be  $8\frac{1}{2}$  in below the top of the shield. There shall be three  $\frac{1}{2}$ -in holes in each of the four sides with their centers 1 in above the base of the shield.

*Type 2 Shield* (Fig. 40-7) is 17½ in. high, 8 in. long, and 8 in. wide, made of sheet metal of approximately 22 gage, with a window on the front side. The open bottom of the shield shall be spaced approximately 2 in. from the base of the unit. The rear of the shield shall have an elliptical hole for the vapor tube. A flask-adjusting knob shall be located on front of the shield for adjusting the flask support. Also, a heat-adjusting indicating dial shall be used to provide stepless heat control when the electric heater is used. The entire mechanism shall be built into the bottom portion of the shield. When an electric heater is employed, the portion of the shield above the board shall be the same as with the gas burner, but the part below may be omitted.

**Heat Source.—Gas Burner** (Fig. 40-6), so constructed that sufficient heat from the available gas can be obtained to distil the product at the specified rate. A sensitive regulating valve and gas pressure governor to give complete control of heating may be provided.

**Electric Heater** (Fig. 40-7) may be used instead of a gas burner, provided it is capable of bringing over the first drop from a cold start within the time specified and of continuing the distillation at the specified rate. Heater units of low heat retention, adjustable from 0 to 1000 watts, have been found satisfactory.

**Flask Support. Type 1 for Use with Gas Burner** (Fig. 40-6).—A ring support of the ordinary laboratory type, 4 in. or larger in diameter, supported on a stand inside the shield or a platform and adjustable from the outside of the shield, may be used.

Two ceramic or hard asbestos boards, ⅛ to ¼ in. in thickness, shall rest upon the ring or the platform, whichever is used. The board immediately above the ring or platform shall have a centered opening 3 to 4 in. in diameter and outside line dimensions slightly smaller than the inside boundaries of the shield.

The second or flask support board shall be slightly smaller in outside dimensions than the first board and shall have a centered opening conforming to the dimensions prescribed in Table 40-8. It shall be ⅛ to ¼ in. in thickness at the center hole rim. This flask support board may be moved slightly in accordance with the directions for placing the distillation flask, and direct heat shall be applied to the flask only through the opening in this board.

**Type 2 for Use with Electric Heater** (Fig. 40-7).—The top of the electric heater shall consist of a ceramic or hard asbestos flask support board with a centered hole

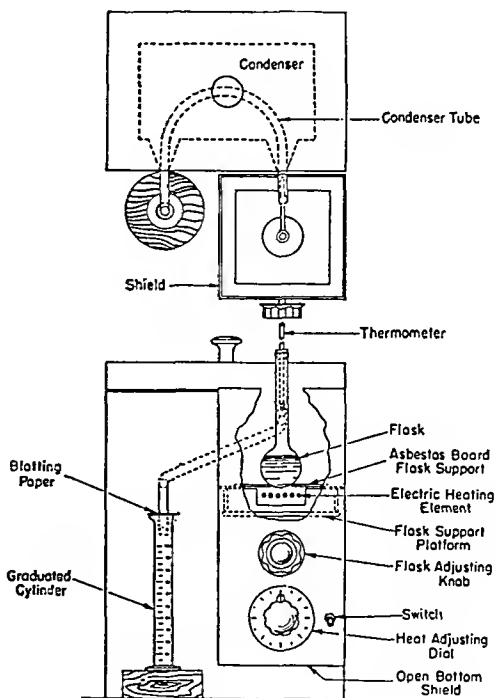


FIG. 40-7. Apparatus Assembly Using Electric Heater.

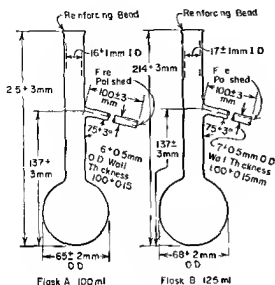
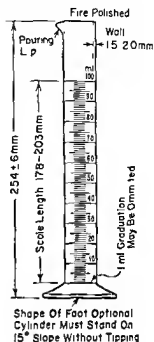


FIG 40 8 Distillation Flasks

FIG 40 9 Graduated Cylinder 100 ml in 1 ml Graduations Tolerance  $\pm 1.0$  ml

as specified in Table 40 8 and a thickness of  $\frac{1}{8}$  to  $\frac{1}{4}$  in at the center hole mm Provision shall be made for moving the heater unit, with its top in order to place the distillation flask so that direct heat shall be applied to the flask only through the opening in the flask support board

TABLE 40 8 FLASK SUPPORT BOARDS

Flask Support Board	Diameter of Opening, in
A	$1\frac{1}{4}$
C	2

Graduated Cylinders—The graduated cylinder is shown in Fig 40 9

Thermometers—Use ASTM thermometers shown in Table 40 9

NOTE—Whenever thermometers complying with ASTM requirements are not available thermometers complying with the requirements applicable to the Institute of Petroleum thermometers IP 5C (low distillation) and IP 6C (high distillation) may be used provided calibration corrections are used in temperature ranges where IP requirements for scale accuracy are less stringent than those of ASTM

TABLE 40-9 THERMOMETERS

ASTM Thermometer No. <sup>a</sup>	Range in Degrees		Sub- divisions
	Fahrenheit	Centigrade	
7F	30 to 580	—	2F
7C	—	-2 to 300	1C
8F	30 to 760	—	2F
8C	—	-2 to 400	1C

<sup>a</sup> The detailed constructional requirements for these thermometers are found in Table I of ASTM Specifications E1.

**Sample.**—In the case of any product having a Reid Vapor Pressure of 9.5 lb. or higher, cool the sample bottle to the temperature range indicated in Table 40-6 for measuring the distillation charge. Collect the sample in the previously cooled bottle, preferably by immersing the bottle in the liquid, where possible, and discarding the first sample. Where immersion is not possible, the sample shall be drawn off into the previously cooled bottle in such a manner that agitation is kept at a minimum. Close the bottle immediately with a tight-fitting stopper, and place it in an ice bath or refrigerator capable of maintaining the sample at a temperature not to exceed 60°F. (15°C.).

Samples of materials that visibly contain water are not suitable for testing. If the sample is not dry, and the initial boiling point is below 150°F. (66°C.), obtain another sample which is free from suspended water for the test. If the initial boiling point is above 150°F. (66°C.), shake the sample with anhydrous sodium sulfate or other suitable drying agent and separate it from the drying agent by decanting.

**Preparation of Apparatus.**—Refer to Table 40-6 and select the flask, flask support, and thermometer, which are required by the sample to be tested. Bring the respective temperatures of the flask, thermometer, graduate, flask support, and shield to their required values for starting the test.

Fill the condenser box to cover the condenser tube with any nonflammable coolant which is suitable for the temperature required by Table 40-6, such as chopped ice, water, brine, or ethylene glycol solution. If chopped ice is used, add sufficient water to cover the condenser tube. If necessary, make any suitable provision, such as circulation, stirring, or air blowing, so as to maintain the required condenser bath temperature throughout the test. Similarly, make any necessary provision so that the temperature of the bath around the graduate will remain within the limits required in Table 40-6.

Remove any residual liquid in the condenser tube by swabbing with a piece of soft, lint-free cloth attached to a cord or copper wire.

Bring the temperature of the sample within the range prescribed in Table 40-6. Measure 100 ml. of the sample in the graduated cylinder and transfer it as com-



pletely as practicable to the distillation flask taking care that none of the liquid flows into the vapor tube

Fit the thermometer provided with a snug fitting well rolled cork tightly into the neck of the flask so that the bulb is centered in the neck and the lower end of the capillary is level with the highest point on the bottom of the inner wall of the vapor tube

Place the flask containing the 100 ml charge in its support and by means of a cork through which the vapor tube has been passed make a tight connection with the condenser tube. Adjust the flask so that it is in a vertical position and so that the vapor tube extends into the condenser tube for a distance of 1 to 2 in

Place the graduate that was used to measure the charge without drying into its bath under the lower end of the condenser tube so that the end of the condenser tube is centered in the graduate and extends therein for a distance of at least 1 in but not below the 100 ml mark. Cover the graduate closely with a piece of blotting paper or similar material suitably weighted which has been cut to fit the condenser tube snugly. Maintain the level of the bath around the graduate so that it is at least as high as the 100 ml mark

Note and record the prevailing barometric pressure and proceed at once with the distillation as directed in the following section

**Procedure**—Apply heat to the distillation flask and contents. The heating at this stage must be so regulated that the time interval between the first application of heat and the initial boiling point does not exceed the limit as prescribed in Table 40 6

Immediately after observing the initial boiling point move the graduate so that the tip of the condenser touches its inner wall. Continue to regulate the heating so that the rate of condensation into the graduate shall be uniform and within the limits prescribed in Table 40 6. Repeat any distillation which did not meet the foregoing conditions

In the interval between the initial boiling point and the end of the distillation observe and record whatever thermometer readings at prescribed percentages recovered and/or percentages recovered at prescribed thermometer readings are necessary for the calculation and reporting of the results of the test as prescribed in the following section. Record all volumes in the graduate to the nearest 0.5 ml and all thermometer readings to the nearest 1.0°F (0.5°C)

**NOTE** In cases in which no specific data requirements have been indicated record the initial boiling point the end point or dry point or both and thermometer readings at 5% and 95% recovered and at each multiple of 10% recovered from 10 to 90% inclusive

If either a thermometer reading of 700°F (371°C) or a decomposition point is observed discontinue the heating and resume the procedure as directed in the third paragraph following (which begins with the words While the condensate tube ) Otherwise proceed according to the following directions

When the residual liquid in the flask is approximately 5 ml make a final adjustment of the heat if necessary so that the time from the 5 ml of liquid residue in the flask to the end point shall meet the requirements given in Table 40 6. If this condition is not satisfied repeat the test with appropriate modification of the final heat adjustment

Observe and record the end point or dry point or both as required and discontinue the heating. At the end point observe if all the liquid has evaporated

from the bottom of the flask. If not, include a note of this fact in the report as prescribed in the following section.

While the condenser tube continues to drain into the graduate, observe the volume of condensate at 2-minute intervals until two successive observations agree. Measure this volume accurately, and record it, to the nearest 0.5 ml., as per cent recovery. If the distillation was previously discontinued under the conditions given in the third paragraph preceding, deduct the per cent recovery from 100, report this difference as "Per Cent Residue and Loss," and omit the procedure given in the next two paragraphs.

After the flask has cooled, pour its contents into the condensate in the graduate and allow to drain until no appreciable increase in the volume of liquid in the graduate is observed. Record this volume, to the nearest 0.5 ml., as per cent total recovery.<sup>8</sup>

Deduct the per cent total recovery from 100 to obtain the per cent loss.

**Calculations and Reporting.**—For each test, calculate and report whatever data are required by the specification involved, or as customarily established for the sample under test, or in accordance with the NOTE above.

Report all percentages to the nearest 0.5%, and all thermometer readings to the nearest 1.0°F. (0.5°C.).

When thermometer 8F (8C) is used in testing aviation turbine fuels and similar products, pertinent thermometer readings may be obscured by the cork. To provide the desired data, a second distillation according to Group 3 of Table 40-6 may have been performed. In such cases, readings from thermometer 7F (7C) may be reported in place of the obscured 8F (8C) readings, and the test report shall so indicate. If, by agreement, the obscured readings are waived, the test report shall so indicate.

When the report is to be based on thermometer readings corrected to 760 mm. barometric pressure (NOTE below), obtain the correction to be applied to each thermometer reading by means of the Sydney Young equation as given below, or by the use of Table 40-10. After applying the corrections and rounding each result to the nearest 1.0°F. (0.5°C.), use the corrected thermometer readings in all further calculations and reporting.

For Centigrade readings:

$$C_c = 0.00012(760 - P)(273 + t_c)$$

For Fahrenheit readings:

$$C_f = 0.00012(760 - P)(460 + t_f)$$

where  $C_c$  and  $C_f$  = corrections to be added algebraically to the observed thermometer readings  $t_c$  or  $t_f$ , respectively. Convenient approximations of these corrections are given in Table 40-10.

$P$  = barometric pressure, millimeters of mercury, prevailing at the time of the test.

**NOTE.**—Care must be taken in all reporting to insure that there will be no question in any case as to whether the Sydney Young correction has or has not been applied to the thermometer readings as reported. In general, these corrections are not applied unless a

<sup>8</sup> As an alternative procedure, drain the cooled liquid remaining in the flask into a small cylinder graduated in 0.1 ml., and observe its volume. Add this observed volume to the per cent recovery, in order to obtain per cent total recovery.

TABLE 40 10 APPROXIMATE CORRECTED THERMOMETER READINGS

Temperature Range		Correction * per 10 mm Difference in Pressure	
Deg Cent	Deg Fahr	Deg Cent	Deg Fahr
10 to 30	50 to 86	0 35	0 63
30 to 50	86 to 122	0 38	0 68
50 to 70	122 to 158	0 40	0 72
70 to 90	158 to 194	0 42	0 76
90 to 110	194 to 230	0 45	0 81
110 to 130	230 to 266	0 47	0 85
130 to 150	266 to 302	0 50	0 89
150 to 170	302 to 338	0 52	0 94
170 to 190	338 to 374	0 54	0 98
190 to 210	374 to 410	0 57	1 02
210 to 230	410 to 446	0 59	1 06
230 to 250	446 to 482	0 62	1 11
250 to 270	482 to 518	0 64	1 15
270 to 290	518 to 554	0 66	1 19
290 to 310	554 to 590	0 69	1 24
310 to 330	590 to 626	0 71	1 28
330 to 350	626 to 662	0 74	1 32
350 to 370	662 to 698	0 76	1 37
370 to 390	698 to 734	0 78	1 41
390 to 410	734 to 770	0 81	1 45

\* To be added in case barometric pressure is below 760 mm to be subtracted in case barometric pressure is above 760 mm

controversy exists or a precision evaluation is desired on data in which the difference in barometric pressures would have a significant effect

After barometric corrections of the thermometer readings have been made if required the following data require no further calculation prior to reporting initial boiling point dry point end point decomposition point per cent recovery per cent total recovery and all pairs of corresponding values involving percentages recovered and thermometer readings Per cent loss and per cent residue are calculated in accordance with their respective definitions as set forth under the definitions on p. 1929

### DISTILLATION OF CRUDE PETROLEUM \*

This method of test is intended for determining the percentages and distillation range of the naphtha in any crude petroleum of the class known commercially as

\* Approved as ASTM D285 54T and ASA No. Z11.32 1955

refinable crude oils. This method does not attempt to specify what quality of product shall be defined as naphtha, nor can it be expected to duplicate the results of commercial refining operations. It specifies apparatus and procedure, leaving selection of numerical limits and interpretation of results to be agreed upon by the interested parties.

**Outline of Method.**—A 500-ml. distillation flask, equipped with a fractionating column, is used to distill one or more 300-ml. portions of sample at a rate of 4 to 5 ml. per min. to a predetermined thermometer reading. (See Fig. 40-10.)

A 100-ml. portion of the total distillate is distilled in accordance with Method D86, Test for Distillation of Petroleum Products (p. 1929).

### APPARATUS

**Distillation Flask.**—A distilling flask conforming to the dimensions and permissible variations indicated in Fig. 40-10.

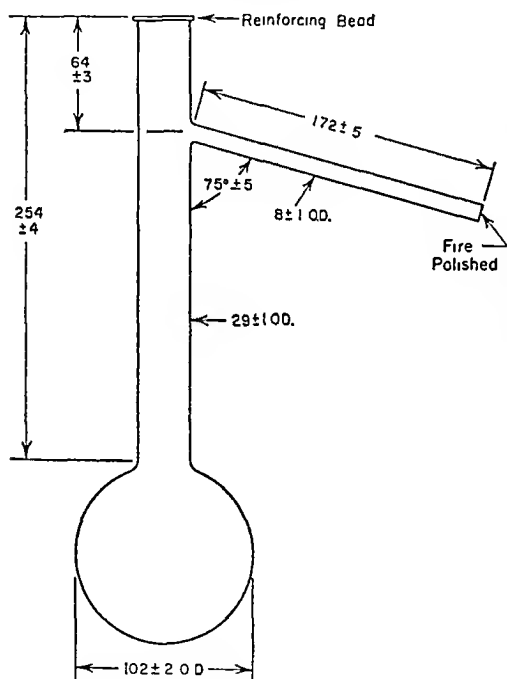


FIG. 40-10. Distillation Flask: All Dimensions in Millimeters.

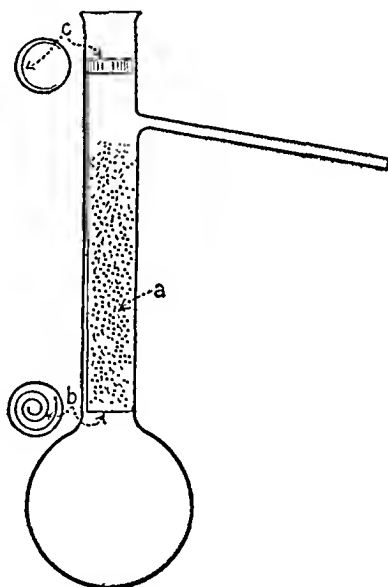


FIG. 40-11. Fractionating Column and Supporting Device in Hemple Flask.

**Fractionating Column.**—A fractionating column (see *a*, Fig. 40-11) made of a length of No. 18 iron jack chain, enough to pack under its own weight, is placed in a column 1 in. in diameter and 6½ in. in length. The jack chain may be "strung" conveniently on a loop of wire so that it hangs in loops about 2 ft. in length, which makes the chain more convenient to handle than when it is not looped together. The device used for supporting the column (see *b*, Fig. 40-11) shall be made of a suitable length of wire, preferably though not necessarily, of nickel-chromium, about No. 18 gage. One end shall be wound in a spiral a little

less than 1 in in diameter and the remaining wire shall be bent at a right angle to the plane of the spiral and cut off at a length of about  $9\frac{1}{2}$  in. A small loop shall be bent into the end away from the spiral and put through a hole drilled in a strip of spring steel (see c, Fig 40 11) or other suitable material about 0.015 in in thickness  $\frac{3}{8}$  in in width and 3 in in length, bent around a cylinder 1 in in diameter. When allowed to expand this spring strip should hold firmly on the inside of the neck of the flask and provide a secure support for the column of chain.

Condenser—A condenser  $\frac{3}{16}$  in in outside diameter, with 0.031 to 0.036 in wall thickness made of seamless brass tubing, 22 in in length. It shall be set so that approximately  $15\frac{1}{2}$  in of the tube will be in contact with the cooling medium contained in the condenser jacket subsequently described, with about 2 in outside the cooling bath at the upper end, and  $4\frac{1}{2}$  in outside the cooling bath at the lower end. The length of tubing projecting at the upper end shall be straight and shall be set at an angle of  $75^\circ$  with the vertical. The section of the tube inside the cooling bath may be either straight or bent in any suitable continuous smooth curve. The average gradient shall be 0.259 in per linear inch of condenser tube (sine of angle of  $15^\circ$ ) and no section of the immersed portion of the condenser tube shall have a gradient less than 0.24 in nor more than 0.28 in per linear inch of tube. The projecting lower portion of the condenser shall be curved downward for a length of 3 in and slightly backward so as to insure contact with the wall of the

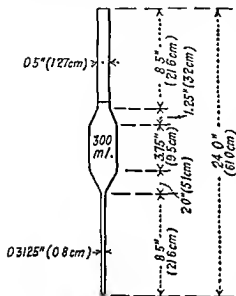


FIG 40 12 Measuring Pipet

receiving graduate at a point approximately 1 to  $1\frac{1}{4}$  in below the top of the graduate when it is in position to receive the distillate. The lower end of the condenser tube shall be cut off at an acute angle. The capacity of the cooling bath shall be not less than 340 cu in (5.55 l) of cooling medium. The arrangement of the tube in the cooling bath shall be such that its center line shall be not less than  $1\frac{1}{4}$  in below the plane of the top of the bath at its point of entrance and not less than  $\frac{3}{4}$  in above the floor of the bath at its exit. Clearance between the condenser tube and the walls of the bath shall be at least  $\frac{1}{2}$  in, except for the sections adjacent to the points of entrance and exit. Multiple installations are permissible, provided they conform to the dimensional requirements and the capacity of the bath is not less than 340 cu in (5.55 l) per tube.

NOTE—A condenser conforming to these requirements is illustrated in Method D-6 (p 1933).

Shield—A shield of any convenient type having a minimum horizontal dimension of 6 in. Except for the vertical dimensions which require modification due to the relatively large flask used in this method, the shield illustrated in Fig 40-7 on page 1933, is satisfactory. When an electric heater is used as the source of heat the part of the shield below the board may be omitted.

**Board and Support.**—The crude oil distilling flask shall rest on a board of approximately  $\frac{1}{4}$ -in. hard asbestos or ceramic material having a hole  $3\frac{1}{2}$  in. in diameter in the center. The board shall not be less than 6 in. in width. When used with a gas burner, the board shall be supported by a ring stand and ring, or other suitable flask support platform.

**Source of Heat.**—Gas burner or electric heater, of sufficient capacity to maintain the distillation rate specified under Procedure, and provided with suitable attachments for close heat control.

**Thermometer.**—ASTM Low Distillation Thermometer graduated in either Fahrenheit or Centigrade degrees as specified, having a range of 30 to 580°F. or -2 to +300°C. and conforming to the requirements for thermometer 7F or 7C, respectively, as prescribed in ASTM Specifications E1.

**NOTE.**—Whenever thermometers complying with ASTM requirements are not available, thermometers complying with the requirements for The Institute of Petroleum thermometer "IP 5C Low Distillation" may be used, provided calibration corrections are used in temperature ranges where IP requirements for scale accuracy are less stringent than those of ASTM.

**Measuring Graduates and Pipet.**—Suitable accurately graduated cylinders or other volumetric glassware for measuring the sample and distillation fractions. A 300-ml. pipet with unconstricted outlet, similar to Fig. 40-12, is a convenient device for measuring charges, but an accurate graduate may be used if desired. The 100-ml. graduate specified on page 1934 is reasonably satisfactory for measuring distillation fractions, but a graduate of similar dimensions that can be stoppered tightly is preferable. One can be made by cutting down a standard graduate to remove the lip and then fire polishing.

**Preparation of Apparatus.**—Fill the condenser bath with cracked ice and add enough water to cover the condenser tube. Maintain the temperature between 32 and 34°F. (0 and 1°C.). Any other convenient cooling medium may be used provided these temperature conditions are maintained.

Swab or clean the inside of the condenser tube to remove any liquid remaining from a previous test.

Measure or weigh a quantity of crude petroleum equivalent to 300 ml., at 60°F. (15.5°C.) into the distillation flask by any suitable means. Do not permit any liquid to flow into the vapor tube (**NOTE**).

**NOTE.**—If the water content of the crude oil causes bumping or, in any case if the crude oil contains more than 2% of water, dehydrate the sample by a suitable method, without loss of naphtha, before making the determination.

Put the supporting device for the fractionating column, Fig. 40-10, in place and carefully drop in the proper quantity of iron jack chain so that it fills the space uniformly and without channels. Tapping the flask while the chain is being added is helpful, but do not compress the column after all the chain is in place.

Fit the thermometer, provided with a cork, tightly into the flask so that it will be in the vertical axis of the neck and so that the lower end of its capillary tube is about  $\frac{1}{16}$  in. (1.5 mm.) below the level of the inside of the bottom of the vapor tube at its juncture with the neck of the flask.

Place the charged flask in position on the hard asbestos or ceramic board and connect it to the condenser with a carefully fitted cork through which the vapor tube passes. Adjust the position of the flask so that the vapor tube extends into the condenser tube not less than 1 in. (2.5 cm.) nor more than 2 in. (5 cm.).

Place a clean dry graduated cylinder at the outlet of the condenser tube in such a position that the condenser tube extends at least 1 in (2.5 cm) into the graduate. Place the graduate in a transparent container and fill this with water to a level of about 1 in (2.5 cm) below the tip of the condenser tube. Maintain the water at 32 to 10°F (0 to 4°C). During the distillation cover the top of the graduate closely with a piece of blotting paper or its equivalent cut to fit the condenser tube tightly.

**Procedure—Crude Oil Distillation**—When everything is in readiness apply heat. Heat may be applied vigorously until the liquid begins to boil then decreased so that the distillate begins to come over at a moderate rate; however when a gas burner is used the flame shall at no time be so large that it spreads over a diameter greater than 5 in (13 cm) on the under surface of the asbestos or ceramic board. Distill the first 5 to 10 ml at the rate of 2 to 3 ml per minute thereafter increase the rate of distillation to 4 to 5 ml per minute.

When the thermometer reads the predetermined temperature (NOTE) withdraw the graduate from beneath the condenser and discontinue the distillation. Stopper the graduate tightly and allow it to stand until all sediment and moisture have settled and until its contents have reached a temperature of 55 to 65°F (13 to 18°C). Read and record the total volume in the graduate and the volume of water if any. Observe and record the barometric pressure.

**NOTE**—The predetermined temperature can best be decided by mutual agreement between the parties concerned in the evaluation of a given crude petroleum. In cases of dispute or when stipulated by the interested parties the effect of variations in barometric pressure on the distillation must be taken into consideration and the distillation is stopped at an adjusted temperature as determined by the following formula which is based on the Sydney Young equation:

$$T_a = t - 0.00012(760 - P)(h + t_a)$$

where  $T_a$  = adjusted predetermined temperature

$t$  = specified predetermined temperature

$P$  = actual barometric pressure in millimeters of mercury,

$h$  = 460 if temperatures are in degrees Fahrenheit or

= 273 if temperatures are in degrees Centigrade

Repeat the whole procedure enough times to yield a total volume of distillate of not less than 100 ml.

**Naphtha Distillation**—Pour the distillates together (taking care to avoid losses by evaporation and rejecting the layers of water if present) and mix thoroughly by shaking. Test the combined distillates in accordance with Method D86 (page 1929) except read and record only the initial boiling point and the volume of distillate collected in the cylinder when the mercury of the thermometer reads 212°F (100°C), 221°F (105°C), 284°F (140°C), 392°F (200°C) and the end point.

**Calculation**—Calculate the percentage of naphtha in the crude oil using the following formula:

$$\text{Naphtha, per cent} = \frac{D - W}{V - W} \times 100$$

where  $D$  = total volume in the graduates,

$W$  = total volume of water in the graduates, and

$V$  = total volume of crude oil charged to the flasks

**Precision.**—Results of duplicate tests in the crude oil distillation should not differ from each other by more than 0.5 per cent.

**Special Procedure for Obtaining Large Volumes of Distillate.**—If it is necessary to obtain quantities of distillate large enough for octane ratings or other special tests, the following procedure may be used: Distill a charge of crude oil in equipment of suitable size to provide the desired amount of naphtha distillate in a single run or in a small number of runs. The equipment shall be so designed and operated that it duplicates both the yield and the quality of the distillate obtained by use of the regular procedure with a 300-ml. charge. Consider the following criteria in deciding whether the two procedures give equivalent results:

- (a) Yields of naphtha distillate shall not differ by more than 1%.
- (b) The distillation curves of the naphtha fractions shall not differ at any point by more than 2.0%.

### SAYBOLT VISCOSITY <sup>10</sup>

This method describes procedures for the empirical measurement of Saybolt viscosity of petroleum products at specified temperatures between 70 and 210°F. There is also included a special procedure for waxy and resinous materials.

**NOTE.**—A fundamental and preferred method for measuring viscosity is by use of kinematic viscometers as outlined in ASTM Method D445, Test for Kinematic Viscosity. This method requires smaller samples, less time, and gives greater accuracy.

Saybolt Universal and Saybolt Furol viscosities may be obtained from kinematic viscosity values by the use of conversion tables given in ASTM Method D446, Conversion of Kinematic Viscosity to Saybolt Universal Viscosity, and ASTM Method D666, Conversion of Kinematic Viscosity to Saybolt Furol Viscosity, respectively.

Viscosity index calculation from kinematic viscosity is recommended over viscosity index calculations using Saybolt Universal values.

Saybolt Furol Viscosity of Asphaltic Materials at High Temperatures is covered by ASTM Method E102.

**Definition.** (a) **Saybolt Universal Viscosity.**—The efflux time in seconds of 60 ml. of sample flowing through a calibrated Universal orifice under specified conditions.

(b) **Saybolt Furol Viscosity.**—The efflux time in seconds of 60 ml. of sample flowing through a calibrated Furol orifice under specified conditions. The Furol viscosity is approximately one-tenth the Universal viscosity, and is recommended for those petroleum products having viscosities greater than 1000 seconds (Saybolt Universal), such as fuel oils, and other residual materials. The word "Furol" is a contraction of fuel and road oils.

**Outline of Method.**—The efflux time in seconds of 60 ml. of sample, flowing through a calibrated orifice, is measured under carefully controlled conditions. This time is corrected by an orifice factor, and reported as the viscosity of the sample at that temperature.

**Apparatus.** **Viscometer and Bath.**—The viscometer, illustrated in Fig. 40-13, shall be constructed entirely of corrosion-resistant metal, conforming to dimensional requirements shown in Fig. 40-13. The orifice tip, Universal or Furol, may be constructed as a replaceable unit in the viscometer. Provide a nut at the lower end of the viscometer for fastening it in the bath. Mount vertically in the bath and test the alignment with a spirit level on the plane of the gallery rim. Provide a

<sup>10</sup> Standardized as ASTM D88-56 and ASA No.: Z11.2-1956.



cork or other suitable means to prevent the flow of sample until the start of the test a small chain or cord may be attached to the cork to facilitate rapid removal

The bath serves both as a support to hold the viscometer in a vertical position as well as the container for the bath medium Equip the bath with effective insulation and with an efficient stirring device Provide the bath with a coil for heating and cooling and with thermostatically controlled heaters capable of maintaining the bath within the functional precision given in Table 40 11 The heaters and coil

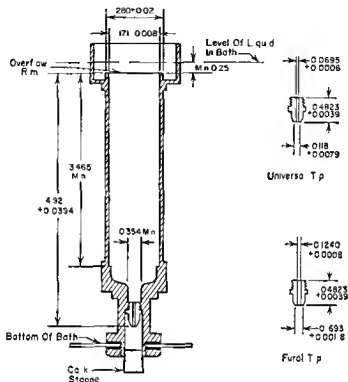


FIG 40 15 Saybolt Viscometer with Universal and Furol Orifice (All Dimensions in Inches)

should be located at least 3 in from the viscometer Provide a means for maintaining the bath medium at least  $\frac{1}{4}$  in above the overflow rim The bath media are given in Table 40 11

Withdrawal Tube as shown in Fig 40 14

Thermometer Support as shown in Fig 40 15

Filter Funnel as shown in Fig 40 16

Receiving Flask as shown in Fig 40 17

Timer, graduated in tenths of a second and accurate to within 0.1 per cent when tested over a 60 min interval Electric timers are acceptable if operated on a controlled frequency circuit

Viscosity Thermometers for reading the test temperature of the sample The ASTM Saybolt Viscosity Thermometers shown in Table 40 12 shall conform to the requirements in ASTM Specifications E1

Bath Thermometers—Viscosity thermometers or any other means of equivalent accuracy

TABLE 40-11 BATH TEST TEMPERATURES

Standard Test Temperature, deg. Fahr.	Recommended Bath Medium	Maximum Temperature Differential, <sup>a</sup> deg. Fahr.	Functional Precision
70	Water.....	±0.1	±0.05
77	Water.....	±0.1	±0.05
100	Water, or Oil of viscosity 50 to 70 sec. S.U. at 100°F.....	+0.25	±0.05
122	Water, or Oil of viscosity 120 to 150 sec. S.U. at 100°F.....	+0.35	±0.05
130	Water, or Oil of viscosity 120 to 150 sec. S.U. at 100°F.....	+0.5	±0.05
140	Water, or Oil of viscosity 120 to 150 sec. S.U. at 100°F.....	+1.0	±0.1
180	Water, or Oil of viscosity 330 to 370 sec. S.U. at 100°F.....	+1.5	±0.1
210	Oil of viscosity 330 to 370 sec. S.U. at 100°F.....	+2.0	±0.1

S.U. = Saybolt Universal.

<sup>a</sup> Maximum difference allowed between bath temperature and test temperature to maintain thermal equilibrium while stirring sample in viscometer with test thermometer.

TABLE 40-12. ASTM SAYBOLT VISCOSITY THERMOMETERS

Standard Test Temperature, deg. Fahr.	Temperature Range, deg. Fahr.	Subdivisions, deg. Fahr.	ASTM Thermometer No.
70	66 to 80	0.2	17F
77	66 to 80	0.2	17F
100	94 to 108	0.2	18F
122	120 to 134	0.2	19F
130	120 to 134	0.2	19F
140	134 to 148	0.2	20F
180	174 to 188	0.2	21F
210	204 to 218	0.2	22F

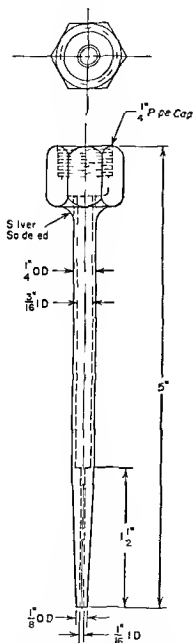


FIG 40 14 Withdrawal Tube for Use with Saybolt Viscometer (All Dimensions in Inches)

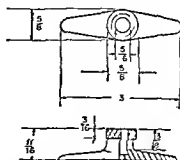


FIG 40 15 Thermometer Support (All Dimensions in Inches)

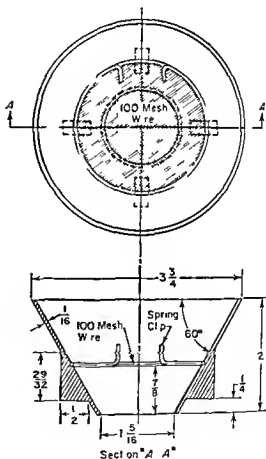


FIG 40 16 Filter Funnel for Use with Saybolt Viscometer (All Dimensions in Inches)

**Preparation of Apparatus.**—Use a Universal orifice for lubricants and distillate materials with efflux times greater than 32 seconds to give the desired accuracy. Liquids with efflux times over 1000 seconds are not conveniently tested with this orifice.

Use a Furol orifice for residual materials with efflux times greater than 25 seconds. The Furol efflux time is approximately one-tenth the Universal efflux time.

NOTE.—The Universal orifice is used at 70, 100, 130, and 210°F. The Furol orifice is used at 77, 100, 122, and 210°F.

Set up the viscometer and bath where they will be free from drafts and rapid changes in air temperature. Locate them so that the sample will not be contaminated by dust or vapors during the test.

Viscosity determinations shall not be made at temperatures below the dew point of the room's atmosphere. Room temperatures up to 100°F. will not introduce errors in excess of 1.0 per cent. For standardization and referee tests, the room temperature shall be kept between 68 and 86°F., and the actual temperature recorded.

Fill the bath at least  $\frac{1}{4}$  in. above the overflow rim of the viscometer. Table 40-12 lists recommended bath media for each test temperature.

Provide adequate stirring and thermal control for the bath so that the sample will not fluctuate more than  $\pm 0.05^\circ\text{F}$ . after reaching the test temperature.

Clean the viscometers with an effective nontoxic solvent and remove all solvent from the gallery and viscometer.

NOTE.—The plunger commonly supplied with the viscometer should never be used for cleaning as the overflow rim and walls of the viscometer may be damaged by its use.

**Calibration of Viscometers.**—Calibrate the Saybolt Universal viscometer at periodic intervals by measuring the efflux time at 100°F. of an appropriate viscosity standard, following the procedure for standards given below.

Viscosity standards are available from two sources. These standards may be used with equal confidence provided they are used immediately after opening and not stored for re-use as permanent viscosity standards.

**Standards Conforming to ASTM Saybolt Viscosity Standards.**—Viscosity Oil Standards conforming to the requirements of ASTM Viscosity Oil Standards for viscometer calibration having certified Saybolt viscosity values established by co-operative determinations of kinematic viscosity values. The kinematic values are converted to Saybolt Universal and Saybolt Furol viscosity values by means of conversion tables given in ASTM Methods D446 and D666, respectively. The Viscosity Oil Standards are oils with approximate Saybolt viscosities as shown in Table 40-13.

**NBS Viscosity Standards.**—National Bureau of Standards liquid viscosity standards having accurate values supplied with each sample. Standard SB has a Saybolt

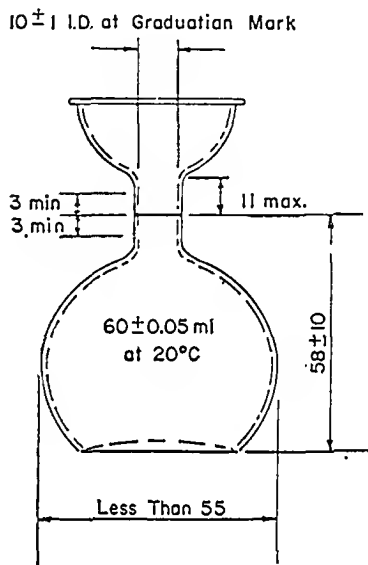


FIG. 40-17. Receiving Flask. (All Dimensions in Millimeters.)

TABLE 40 13 SAYBOLT VISCOSITY STANDARDS <sup>a</sup>

Viscosity Oil Standards Conforming to ASTM Standards	Approximate Saybolt Viscosity, sec		
	Universal		Furol At 122°F
	At 100°F	At 210°F	
S3	36	—	—
S6	46	—	—
S20	100	—	—
S60	290	—	—
S200	970	—	—
S600	—	150	133

<sup>a</sup> These are approximate values only. Certified values are supplied with each shipment. These viscosity oil standards are available as 1 pt samples at \$15.00 per sample FOB State College, Pa. Purchase orders should be addressed to the Cannon Instrument Co., P. O. Box 812, State College, Pa. Shipment will be made as specified or by best means.

Universal viscosity of approximately 300 sec at 100°F. Standard SF has a Saybolt Furol viscosity of approximately 100 seconds at 122°F.

NOTE: The NBS viscosity standards are available only as 1 pt samples at \$6.00 per sample FOB Washington, D. C. Purchase orders should be addressed to the National Bureau of Standards, Washington 25, D. C.

**Routine Calibrations**—The viscosity standards may also be used for routine calibrations at other temperatures as shown in Table 40 13.

**Other Viscosity Standards**—Other reference liquids suitable for routine calibrations may be established by selecting stable oils covering the desired range and determining their viscosities in a viscometer calibrated with a standard conforming to ASTM requirements or an NBS standard as described herein.

The efflux time should equal the certified Saybolt viscosity value. If the efflux time differs from the certified value by more than 0.2%, calculate a correction factor  $F$  for the viscometer as follows:

$$F = \frac{V}{t}$$

where  $V$  = certified Saybolt viscosity of the standard, and  
 $t$  = efflux time in seconds at 100°F

NOTE—The correction factor applies at all viscosity levels and for all temperatures provided the calibration is based on a viscosity standard having an efflux time between 200 and 600 sec.

Calibrate the Saybolt Furol viscometer at 122°F in the same manner as above using a viscosity standard having a minimum efflux time of 90 seconds.

Viscometers or orifices which have corrections in excess of 1.0 per cent shall not be used for referee testing.

**Procedure.**—If the test temperature is above room temperature, the test may be expedited by preheating the sample to not more than 3°F. above the test temperature. Never preheat any sample to within 50°F. of its flash point (see ASTM Method D93, Test for Flash Point by Means of the Pensky-Martens Closed Tester), as volatility losses may alter its composition.

Insert a cork stopper, having a cord attached for its easy removal, into the air chamber at the bottom of the viscometer. The cork shall fit tightly enough to prevent the escape of air, as evidenced by the absence of oil on the cork when it is withdrawn.

Filter the prepared sample through a 100-mesh screen directly into the viscometer until the level is above the overflow rim.

Stir the sample until its temperature remains constant within 0.05°F. of the test temperature during 1 minute of continuous stirring. Stir with a viscosity thermometer equipped with a thermometer support (Fig. 40-15). Use a circular motion at 30 to 50 r.p.m. in a horizontal plane.

**NOTE.**—Never adjust the temperature by immersing hot or cold bodies into the sample. Such thermal treatment may affect the sample and the precision of the test.

Remove the thermometer from the sample. Quickly remove the oil from the gallery until its level is below the overflow rim. This is done by placing the tip of the withdrawal tube (Fig. 40-14) at one point in the gallery and applying suction. Do not touch the overflow rim with the withdrawal tube, or the effective head of the sample will be reduced.

Place the receiving flask (Fig. 40-17) where the stream of oil from the bottom of the viscometer will just strike the neck of the flask. The graduation mark on the flask shall be between 10 and 13 cm. from the bottom of the viscometer tube.

Snap the cork from the viscometer using the attached cord. At the same instant start the timer. Stop the timer the instant the bottom of the meniscus reaches the graduation mark. Record the efflux time in seconds.

**Special Procedure for Waxy or Resinous Materials.**—Steam-refined cylinder oils, black lubricating oils, residual fuel oils, and other materials which may possibly contain waxes or resins require special handling to obtain reproducible results. In order to control the possible anomalies in testing such material, the thermal history of the sample shall be controlled. This special procedure will aid in the control of wax crystals and lattice structure formations.

Heat a representative, homogeneous sample in a loosely stoppered container for 1 hour in an oven maintained at 212 to 215°F.

Immediately filter the preheated sample through a 100 mesh screen directly into the viscometer. Place a thermometer with support into the sample. Do not disturb the sample until it is 1°F. above test temperature.

When the sample reaches this temperature, stir it with the thermometer using a circular motion, at 30 to 50 r.p.m., until the temperature of the sample remains constant within 0.05°F. of the test temperature during 1 minute of continuous stirring.

Complete the test as described in the last three paragraphs of preceding section.

Viscosity determinations of these materials shall be completed within 1 hour after filling the viscometer with sample. Do not run repeat determinations on the same portion of these materials.

Hydrometer Cylinders, of metal, clear glass, or plastic. For convenience in pouring, the cylinder may have a lip on the rim. The inside diameter of the cylinder shall be at least 25 mm. greater than the outside diameter of the hydrometer used in it. The height of the cylinder shall be such that the length of the column of sample it contains is greater by at least 25 mm. than the portion of the hydrometer which is immersed beneath the surface of the sample.

*Temperature of Test.*—The gravity determined by the hydrometer method is most accurate at or near the standard temperature of 60°F. Use this or any other temperature between 0 and 195°F. for the test, so far as it is consistent with the type of sample and necessary limiting conditions shown in Table 40-15.

TABLE 40-15. LIMITING CONDITIONS AND TEST TEMPERATURES

Sample Type	Gravity Limits	Initial Boiling Point Limits	Other Limits	Test Temperature
Highly volatile.....	Lighter than 0.70 sp. gr.	—	—	Cool to 35°F. or lower in original closed container
Moderately volatile.....	Heavier than 0.70 sp. gr.	Below 250°F.	—	Cool to 65°F. or lower in original closed container
Moderately volatile and viscous	Heavier than 0.70 sp. gr.	Below 250°F.	Viscosity too high at 65°F.	Heat to minimum temperature for sufficient fluidity
Nonvolatile.....	Heavier than 0.70 sp. gr.	Above 250°F.	—	Any temperature between 0 and 195°F. as convenient
Mixtures of nonpetroleum with petroleum products.....	—	—	—	60 ± 0.25°F.

*Procedure.*—Adjust the temperature of the sample in accordance with Table 40-15. The hydrometer cylinder and thermometer shall be at approximately the same temperature as the sample to be tested.

Pour the sample into the clean hydrometer jar without splashing, so as to avoid the formation of air bubbles and to reduce to a minimum the evaporation of the lower-boiling constituents of the more volatile samples. For the more volatile samples, transfer to the hydrometer cylinder by siphoning. Remove any air bubbles formed, after they have collected on the surface of the sample, by touching them with a piece of clean filter paper before inserting the hydrometer. Place the cylinder containing the sample in a vertical position in a location free from air currents. Take precautions to prevent the temperature of the sample from changing appreciably during the time necessary to complete the test. During this period,

the temperature of the surrounding medium should not change by more than 5°F.

Lower the hydrometer gently into the sample and when it has settled depress it about two scale divisions into the liquid and then release it. Keep the rest of the stem dry. As uncles in liquid on the stem changes the effective weight of the instrument and so affects the reading obtained. With samples of low viscosity a slight spin imparted to the instrument on releasing assists in bringing it to rest floating freely away from the walls of the hydrometer cylinder. Allow sufficient time for the hydrometer to become completely stationary and for all air bubbles to come to the surface. This is particularly necessary in the case of the more viscous samples.

When the hydrometer has come to rest floating freely and the temperature of the sample is constant to 0.2°F read the hydrometer to the nearest scale division. The correct reading is that point on the hydrometer scale at which the surface of the liquid cuts the scale. Determine this point by placing the eye slightly below the level of the liquid and slowly raising it until the surface first seen is a distorted ellipse appears to become a straight line cutting the hydrometer scale.

To make a reading with nontransparent oils observe the point on the hydrometer scale to which the sample rises above its main surface placing the eye slightly above the plane surface of the liquid. This reading requires a correction. Determine this correction for the particular hydrometer in use by observing the height above the main surface of the liquid to which the oil rises on the hydrometer scale when the hydrometer in question is immersed in a transparent oil having a surface tension similar to that of the sample under test.

Observe the temperature of the sample to the nearest 0.2°F immediately before and after the observation of the gravity, the liquid in the cylinder being thoroughly but cautiously stirred with the thermometer, the whole of the mercury thread being immersed. Should these temperature readings differ by more than 1°F repeat the temperature and gravity observations when the temperature of the sample has become more stable. Record the mean of the thermometer reading before and after the final hydrometer reading to the nearest degree Fahrenheit as the temperature of the test.

**Calculation**—When gravities have been observed on opaque liquids by the procedure given in the preceding section add the correction for specific gravity to the hydrometer reading observed.

Correct all hydrometer readings to 60°F using Table 23. Reduction of Observed Specific Gravity to Specific Gravity 60/60°F, of the ASTM IP Petroleum Measurement Tables (American Edition).<sup>22</sup>

**NOTE**—The interconversion of specific gravity to API gravity is given in Table 21. Specific Gravity 60/60°F to Density at 15°C. and to API Gravity at 60°F of the ASTM IP Petroleum Measurement Tables (American Edition).

Equivalent results can be obtained by determining API Gravity at 60°F according to Method D287 (p. 1926) and converting the result to specific gravity 60/60°F by means of Table 3 of the ASTM IP Petroleum Measurement Tables (American Edition).

<sup>22</sup> Published jointly by and available from the American Society for Testing and Materials, 1916 Race St., Philadelphia 3 and the Institute of Petroleum, 26 Portland Place, London W. 1. Companion volumes—the British Edition and the Metric Edition—are also available. These tables supersede all other similar tables previously published by either of these Societies and the National Bureau of Standards Circular C 410 and the Supplement to Circular C 410.



**Precision.**—The following criteria should be used for judging the acceptability of results obtained at temperatures differing from 60°F. by less than 18°F.:

	<i>Repeatability</i>	<i>Reproducibility</i>
	<i>Duplicate Results by the Same Operator</i>	<i>Average of Two Results in Each of Two Laboratories</i>
Specific gravity . . .	0.0015	0.0040

## VAPOR PRESSURE OF PETROLEUM PRODUCTS<sup>13</sup> (REID METHOD)

This method of test covers the determination of the absolute vapor pressure (NOTE 1) of volatile crude oil and volatile nonviscous petroleum products, except liquefied petroleum gases (NOTE 2).

NOTE 1.—Because the external atmospheric pressure is counteracted by the atmospheric pressure initially present in the air chamber, the “Reid vapor pressure” is approximately the vapor pressure of the material at 100°F. in pounds per square inch absolute.

NOTE 2.—For determination of the vapor pressure of liquefied petroleum gases reference should be made to ASTM Method D1267.

**Summary of Method.**—The gasoline chamber of the vapor pressure apparatus is filled with the chilled sample and connected to the air chamber at 100°F. or other temperature. The apparatus is immersed in a constant temperature bath ( $100 \pm 0.2^\circ\text{F}$ .) and is shaken periodically until equilibrium is reached. The “manometer reading” corresponding to the pressure, read on the gage attached to the apparatus, suitably corrected (Table 40-16, p. 1960) if the air chamber was initially at a temperature other than 100°F., is the *Reid vapor pressure*.

This method provides for partial air saturation of products with Reid vapor pressure below 26 lb., for no air saturation for products above 26 lb. and for narrower tolerances in certain features for the measurement of the vapor pressure of aviation gasolines.

**Apparatus.**—The construction of the required apparatus is described below. For samples having vapor pressures below 26 lb., use the gasoline chamber with one opening and for samples having vapor pressures above 26 lb., use the gasoline chamber with two openings.

**Reid Vapor Pressure Bomb**, consisting of two chambers—an air chamber (upper section) and a gasoline chamber (lower section)—shall conform to the following requirements:

**Air Chamber.**—The upper section or air chamber, as shown in Fig. 40-18, should be a cylindrical vessel  $2 \pm \frac{1}{8}$  in. in diameter and  $10 \pm \frac{1}{8}$  in. in length, inside dimensions, with the inner surfaces of the ends slightly sloped to provide complete drainage from either end when held in a vertical position. On one end of the air chamber, a suitable gage coupling with an internal diameter not less than  $\frac{3}{16}$  in. should be provided to receive the  $\frac{1}{4}$ -in. gage connection. In the other end of the air chamber an opening approximately  $\frac{1}{2}$  in. in diameter should be provided for coupling with the gasoline chamber. Care should be taken that the connections to the end openings do not prevent the chamber from draining completely.

<sup>13</sup> Standardized as ASTM D323-58 and ASA No.: Z11.44-1958.

**Gasoline Chamber (One Opening)**—The lower section or gasoline chamber as shown in Fig 40 18 should be a cylindrical vessel of the same inside diameter as the air chamber and of such volume that the ratio of the volume of the air chamber to the volume of the gasoline chamber should be between the limits of 3.8 and 4.2 (see NOTE) In one end of the gasoline chamber an opening approximately  $\frac{1}{2}$  in

diameter should be provided for coupling with the air chamber The inner surface of the end containing the coupling member should be sloped to provide complete drainage when inverted The other end of the gasoline chamber should be completely closed

NOTE—The ratio for units to be used for aviation gasoline testing should be 3.9 to 4.0

**Gasoline Chamber (Two Opening)**—For sampling from closed vessels the lower section or gasoline chamber as shown in Fig 40 18 should be essentially the same as the gasoline chamber described above except that a  $\frac{1}{4}$  in valve should be attached near the bottom of the gasoline chamber and a  $\frac{1}{2}$ -in straight through full opening valve should be introduced in the coupling between the chambers The volume of the gasoline chamber including only the capacity enclosed by the valves should fulfill the volume ratio requirements as set forth above

NOTE—In determining capacities for the two opening gasoline chamber (Fig 40 18) the capacity of the gasoline chamber should be considered as that below the  $\frac{1}{4}$  in valve closure The volume above the  $\frac{1}{2}$  in valve closure including the portion of the coupling permanently attached to the gasoline chamber should be considered as a part of the air chamber capacity

**Method of Coupling Air and Gasoline Chambers**—Any method of coupling the air and gasoline chambers may be employed provided that no gasoline is lost during the coupling operation that no compression effect is caused by the act of coupling and that the assembly is free from leaks under the conditions of the tests To avoid displacement of gasoline during assembly it is desirable that the male fitting of a suitable coupling be on the gasoline chamber To avoid compression of air during the assembly of a suitable screw coupling a vent hole may be used to insure atmospheric pressure in the air chamber at the instant of sealing

**Volumetric Capacity of Air and Gasoline Chambers**—In order to ascertain if the volume ratio of the chambers is between the specified limits of 3.8 to 4.2 a quantity of water greater than will be needed to fill the gasoline and air chambers should be measured The gasoline chamber should be completely filled with water and the difference between the original volume and the remaining volume is the volume of the gasoline chamber Then after connecting the gasoline and air chambers the air chamber should be filled to the seat of the gage connection with more of the

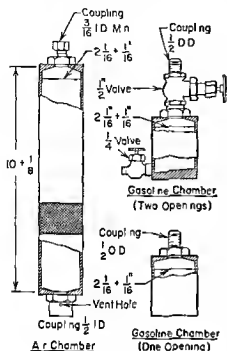


FIG 40 18 Vapor Pressure Bomb (All Dimensions in Inches)

measured water, and the difference in volumes shall be the volume of the air chamber.

*Checking for Freedom from Leaks.*—Before placing new apparatus in service and as often as necessary thereafter, the assembled vapor pressure apparatus should be checked for freedom from leaks by filling with air to 100-psi gage pressure and completely immersing in a water bath. Only apparatus which stands this test without leaking should be used.

*Pressure Gage.*—The pressure gage should be a Bourdon-type spring gage of test gage quality  $4\frac{1}{2}$  to  $5\frac{1}{2}$  in. in diameter provided with a nominal  $\frac{1}{4}$ -in. male thread connection with a passageway not less than  $\frac{3}{16}$  in. in diameter from the Bourdon tube to the atmosphere. The range and graduations of the pressure gage used should be governed by the vapor pressure of the sample being tested, as follows:

Reid Vapor Pressure, lb.	Gage to be Used		
	Scale Range, psi	Maximum Numbered Intervals, psi	Maximum Intermediate Graduations, psi
4 and under.....	0 to 5	1	0.1
3 to 12.....	0 to 15	3	0.1
10 to 26.....	0 to 30	5	0.2
10 to 36.....	0 to 45	5	0.2
30 to 55.....	0 to 60	10	0.25
50 and higher.....	0 to 100	10	0.5

Only accurate gages shall be continued in use. When the gage reading differs from the manometer (or dead-weight tester when testing gages above 26 lb.) reading by more than 1% of the scale range of the gage, the gage should be considered inaccurate. For example, the calibration correction should not be greater than 0.15 psi for a 0 to 15 psi gage or 0.3 psi for a 0 to 30 psi gage.

NOTE.—Gages  $3\frac{1}{2}$  in. in diameter may be used in the 0 to 5 lb. range.<sup>14</sup>

*Water Cooling Bath.*—A water cooling bath shall be provided of such dimensions that the sample containers and gasoline chambers may be completely immersed. Means for maintaining the bath at a temperature of 32 to 40°F. should be provided.

NOTE.—Solid carbon dioxide should not be used to cool samples in storage or in the preparation of the air saturation step. Carbon dioxide is appreciably soluble in gasoline, and its use has been found to be the cause of erroneous vapor pressure data.

*Water Bath.*—The water bath should be of such dimensions that the vapor pressure apparatus may be immersed to at least 1 in. above the top of the air chamber. Means for maintaining the bath at a constant temperature of  $100 \pm 0.2^\circ\text{F}$ . should

<sup>14</sup> Suitable gages are available from the Fisher Scientific Co. (Special Order), Pittsburgh, Pa. and U. S. Gauge Co. (Catalogue No. 510SP), Sellersville, Pa.

be provided. In order to check this temperature the bath thermometer shall be immersed to the 98 F mark throughout the vapor pressure determination.

**Thermometers** For 100°F Air Chamber Procedure—An ASTM Reid Vapor Pressure Thermometer No. 18F having a range of 94 to 108°F and conforming to the requirements in ASTM Specifications E1.

For Water Bath—Use the ASTM thermometer 18F described above.

**For Air Chamber** When the ambient temperature procedure is employed a thermometer conforming to the following requirements shall be used. Length approximately 12 in. range -40 or -30 F to +120 or +130°F graduated in 1°F divisions. total immersion scale error not greater than 1°F.

**Mercury Manometer** A mercury manometer having a range suitable for checking the pressure gage employed shall be used. The manometer scale may be graduated in steps of 1 mm, 0.1 in. or 0.1 psi.

**Dead Weight Tester**—A dead weight tester may be used in place of the mercury manometer for checking gage readings above 26 lb.

**Handling of Samples**—The general provisions in the following paragraphs should apply to all samples for vapor pressure determinations except as specifically excluded for samples having vapor pressures above 26 lb. The extreme sensitivity of vapor pressure measurements to losses through evaporation and to slight changes in composition is such as to require the utmost precaution and the most meticulous care in the handling of samples.

Sampling should be done in accordance with the procedure for Reid vapor pressure as described in ASTM Method D270 Sampling Petroleum and Petroleum Products.

**Sample Container Size**—The size of the sample container from which the vapor pressure sample is taken should be not less than 1 qt. nor more than 2 gal.

**Sample Handling Temperature**—In all cases the sample container and its contents should be cooled to 32 to 40°F before the container is opened.

**Sample Transfer**—The Reid vapor pressure determination should be the first test run on a sample. In the instances of transfer of liquids from larger sample containers or of withdrawal of samples for other tests the transfer connection of Fig. 40-19 should be used.

**Care of Samples**—Samples should be put in a cool place as soon as possible after they have been obtained and held there until the test has been completed. Samples in leaky containers should not be considered for tests but shall be discarded and new samples obtained.

**Preparation for Test** *Air Saturation of Sample in Sample Container*—When the sample at a temperature of 32 to 40°F take the container from the cooling bath, unseal it and examine it for its liquid content which shall be between 70 and 80 per cent of the container capacity. After the correct liquid content has been assured, reseal the container, shake it vigorously and return it to the cooling bath.

**Preparation of Gasoline Chamber**—Completely immerse the open gasoline chamber and the sample transfer connection in the cooling bath for a sufficient time to allow the chamber and connection to reach the bath temperature (32 to 40°F).

**Preparation of Air Chamber (100°F Procedure)**—After purging and rinsing the air chamber and pressure gage in accordance with directions on Preparation of Sample for Next Test page 1958, connect the gage to the air chamber. Immerse the air chamber to at least 1 in. above its top in the water bath maintained at  $100 \pm 0.2^\circ\text{F}$  for not less than 10 minutes just before coupling it to the gasoline chamber. Do not remove the air chamber from the bath until the gasoline chamber has been filled with sample as described under Sample Transfer, page 1957.

**Preparation of Air Chamber (Ambient Temperature Procedure).**—As an alternate to preceding paragraph, the air chamber may be adjusted to ambient or other temperature which may be determined with an accuracy of at least 1°F. in the following manner: After purging and rinsing the air chamber and pressure gage in accordance with directions on Preparation of Sample for Next Test, page 1958, connect the gage to the air chamber. Insert the thermometer into the air chamber, supporting it by means of a loosely-fitting (not air-tight) stopper in the opening of the air chamber. Adjust the position of the thermometer so that it is aligned as closely as possible with the axis of the air chamber, and with the thermometer bulb located in the air chamber, about 9 in. from the opening. Leave the ther-

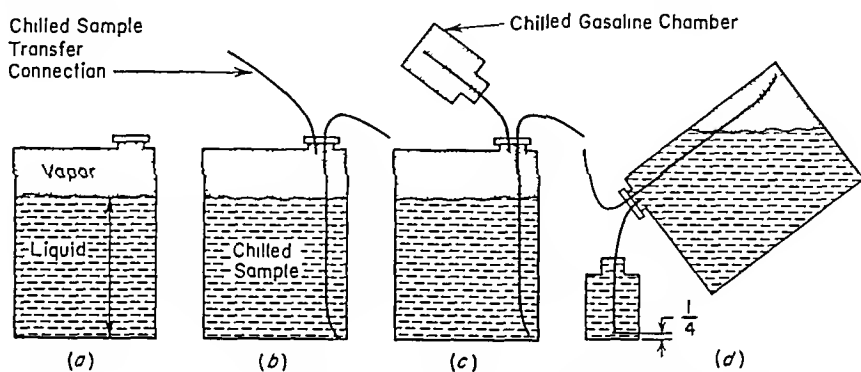


FIG. 40-19. Simplified Sketches Outlining Method of Transferring Sample to Gasoline Chamber from Open-Type Containers: (a) Sample Container Prior to Transfer of Sample; (b) Sealing Closure Replaced by Sample Transfer Connection; (c) Gasoline Chamber Placed Over Liquid Delivery Tube; (d) Position of System for Sample Transfer.

mometer in position until the temperature reading has remained constant within 1°F. for a period of 5 minutes or more just before coupling the air chamber to the gasoline chamber. At this time, record the thermometer reading as the "initial air temperature."

**Procedure. Sample Transfer.**—With everything in readiness, remove the chilled sample container from the bath, uncup it, and insert the chilled transfer connection and air tube (see Fig. 40-19). Then place the empty chilled gasoline chamber over the sample delivery tube of the transfer connection. Invert the entire system rapidly so that the gasoline chamber is finally in an upright position with the delivery tube extending to within  $\frac{1}{4}$  in. of the bottom of the gasoline chamber. Fill the gasoline chamber to overflowing. Lightly tap the gasoline chamber against the work bench to insure that the sample is free of air bubbles. If any sample is displaced, refill the chamber to overflowing.

**Assembly of Apparatus.**—Without delay, and as quickly as possible, attach the air chamber to the gasoline chamber. Not more than 20 seconds shall be consumed in completing the assembly of the apparatus after filling the gasoline chamber, using the following sequence of operations:

1. Refill the gasoline chamber to overflowing,
2. Read the "initial air temperature" or remove the air chamber from the 100°F. water bath, and
3. Connect the air chamber to the gasoline chamber.

**Introduction of Apparatus into Bath** Turn the assembled vapor pressure apparatus upside down to allow the sample in the gasoline chamber to run into the air chamber and shake vigorously in a direction parallel to the length of the apparatus. Immerse the assembled apparatus in the bath maintained at  $100 \pm 0.2^\circ\text{F}$  in an inclined position so that the connection of the gasoline and air chambers is below the water level and may be observed closely for leaks. If no leaks are observed immerse the apparatus to at least 1 in. above the top of the air chamber. Observe the apparatus for leaks throughout the test. When at any time a leak is detected discard the test.

**NOTE**—Liquid leaks are more difficult to detect than vapor leaks and because the much used coupling device is normally in the liquid section of the apparatus give it particular attention.

**Measurement of Vapor Pressure**—After the assembled vapor pressure apparatus has been immersed in the bath for 5 minutes tap the pressure gage lightly and observe the reading. Withdraw the apparatus from the bath invert it shake it vigorously and replace it in the bath in the shortest possible time to avoid cooling the apparatus. At intervals of not less than 2 minutes repeat this agitation and gage observation at least five times until the last two consecutive gage readings are constant to insure equilibrium. These operations normally require 20 to 30 minutes. Read the final gage pressure to the nearest 0.05 lb. for gages with intermediate graduations of 0.1 psi and to the nearest 0.1 lb. for gages with graduations of 0.2 to 0.5 psi and record this value as the uncorrected vapor pressure of the sample under test. Immediately remove the pressure gage and check its reading against that of the manometer recording the value found as the Reid vapor pressure (under the Preparation of Air Chamber ( $100^\circ\text{F}$  Procedure) on p. 1956) or as the manometer reading to be used in the calculations below (under the Preparation of Air Chamber (Ambient Temperature Procedure) on p. 1957).

**Preparation of Apparatus for Next Test**—Disconnect the air chamber gasoline chamber and pressure gage (NOTE 1). Remove trapped fluid in the Bourdon tube by repeated centrifugal thrusts. This may be accomplished in the following manner: hold the gage between the palms of the hands with the right hand on the face side and the threaded connection of the gage forward. Extend the arms forward and upward at an angle of  $45^\circ$  with the coupling of the gage pointing in the same direction. Swing the arms downward through an arc of about  $135^\circ$  so that the centrifugal force aids gravity in removing the trapped liquid. Repeat this operation three times to expel all liquid. Tunge the pressure gage by, attaching a small jet of air into its Bourdon tube for at least 5 minutes. Thoroughly purge the air chamber of residual sample by filling the air chamber with warm water (above  $90^\circ\text{F}$ ) and allowing it to drain (NOTE 2). Repeat this purging at least five times. After thoroughly removing the previous sample from the gasoline chamber immerse the chamber in the ice bath for the next test.

**NOTE 1**—In the case of crude oil the Bourdon tube must be washed with a volatile solvent after each test.

**NOTE 2**—If the purging of the air chamber is done in a bath be sure to avoid small and unnoticed films of floating sample by keeping the bottom and top openings of the chambers closed as they pass through the surface of water.

**Precautions**—Gross errors can be obtained in vapor pressure measurements if the prescribed procedure is not followed carefully. The following list emphasizes the importance of strict adherence to the precautions given in the procedure.

*Checking the Pressure Gage.*—Check all gages against a manometer after each test in order to insure higher precision of results (see Measurement of Vapor Pressure, above). Read all gages while the gage is in a vertical position.

*Air Saturation of Sample.*—Open and close the sample container once after the contents have reached a temperature of 32 to 40°F. Shake the container vigorously to insure equilibrium of the sample with the air in the container (see Air Saturation of Sample in Sample Container, p. 1956).

*Checking for Leaks.*—Check all apparatus before and during each test for liquid and vapor leaks (see Checking for Freedom from Leaks, p. 1955).

*Sampling.*—Because initial sampling and the handling of samples will greatly affect the final results, employ the utmost precaution and the most meticulous care to avoid losses through evaporation and slight changes in composition (see Handling of Samples, p. 1956). In no case shall any part of the Reid apparatus itself be used as the sample container previous to actually conducting the test.

*Purging the Apparatus.*—Thoroughly purge the pressure gage, the gasoline chamber, and the air chamber to be sure that they are free of residual sample. (This is most conveniently done at the end of the previous test.) (Preparation of Apparatus for Next Test, p. 1958).

*Coupling the Apparatus.*—Carefully observe the requirements of Assembly of Apparatus, p. 1957.

*Shaking the Apparatus.*—Shake the apparatus “vigorously” as directed in Measurement of Vapor Pressure, p. 1958, in order to insure equilibrium.

*Temperature Control.*—Carefully control the temperature at the time of air saturation and the temperature of the 100°F. bath (see Water Bath and Water Cooling Bath, p. 1955). Be certain that the temperature of the air in the air chamber at the time of coupling with the gasoline chamber (see Assembly of Apparatus, p. 1957) has remained constant within 1°F. for a period of 5 minutes or more.

*Calculation. Change in Pressure of Water Vapor and Air.*—For the ambient temperature procedure described under Preparation of Air Chamber (Ambient Temperature Procedure, p. 1957, calculate the “Reid vapor pressure” of the sample under test by applying to the “manometer reading” the correction given in Table 40-16 for the change in pressure of the water vapor and air in the chamber on heating from the “initial air temperature” to 100°F.

*Recording Results.*—If the 100°F. Procedure was employed (p. 1956), record the result observed in Measurement of Vapor Pressure, p. 1958, as the “Reid vapor pressure” in pounds without reference to temperature or to unit of surface. If the ambient temperature procedure was used, record the value resulting from the application of the correction from Change of Pressure of Water Vapor and Air, above, as the “Reid vapor pressure” without reference to temperature or unit of surface.

## MODIFICATIONS FOR PRODUCTS HAVING REID VAPOR PRESSURES ABOVE 26 POUNDS

With products having vapor pressures over 26 lb. (NOTE), the procedure described in the foregoing sections is hazardous and inaccurate. Consequently, the following sections define changes in apparatus and procedure for the determination of vapor pressures above 26 lb. Except as specifically stated, all the requirements of the foregoing sections shall apply.

TABLE 40-16 CORRECTIONS TO BE SUBTRACTED FROM "MANOMETER READINGS" FOR CALCULATING REID VAPOR PRESSURE

Initial Air Temperature, <sup>a</sup> deg Fahr	Barometric Pressure, <sup>a</sup> mm		
	760	700	600
32	2 90	2 70	2 45
40	2 60	2 45	2 20
50	2 20	2 10	1 90
60	1 80	1 70	1 55
70	1 40	1 30	1 20
80	0 95	0 90	0 85
90	0 50	0 50	0 45
100	0 00	0 00	0 00
110	-0 55	-0 55	-0 50

<sup>a</sup> For other temperatures and pressures, the corrections may be calculated by means of the following equation

$$\text{Correction} = \frac{(P - P_t)(t - 100)}{460 + t} - (P_{100} - P_t)$$

where  $t$  = air chamber temperature at beginning of test, in degrees Fahrenheit,

$P$  = barometric pressure, in pounds per square inch, at time of test (if a barometer is not available, the normal barometric pressure may be used),

$P_t$  = vapor pressure of water, in pounds per square inch absolute, at  $t$  deg Fahr, and

$P_{100}$  = vapor pressure of water, in pounds per square inch absolute, at 100° F = 0 95

Calculated corrections are to be rounded off to the nearest 0 05 lb

*Example*—The pressure gage gives an "uncorrected vapor pressure" reading of 11 6 lb. When the gage is compared to a mercury column, a "manometer reading" of 11 5 lb is obtained. For an "initial air temperature" of 80° F and atmospheric pressure of 700 mm, the correction shown in Table 40-16 is 0 90 lb. Because the "initial air temperature" is below 100° F, this correction of 0 90 lb is subtracted from the "manometer reading" of 11 5 lb, giving a "Reid vapor pressure" of 10 60 lb.

**NOTE**—When the question arises the air saturation method shall be used to determine whether or not a product has a vapor pressure above 26 lb.

**Apparatus Bomb**—As described on page 1953, using the gasoline chamber with two openings.

**Pressure Gage Calibration**—A dead weight tester (p 1956) may be used in place of the mercury manometer for checking gage readings above 26 lb. On pages 1958 and 1959 and Table 40 16 where the words "manometer" and "manometer reading" appear, include as an alternate "dead weight tester" and "calibrated gage reading" respectively.

**Handling of Samples**—The directions for sample container size, handling temperature, and transfer on p 1956 do not apply.

**Sample Container Size**—The size of the sample container from which the vapor pressure sample is taken shall not be less than 1 pt liquid capacity.



*Preparation for Test.*—The directions for air saturation of sample and chamber preparation on p. 1956 do not apply.

Any safe method of displacement of the test sample from the sample container that assures filling the gasoline chamber with a chilled, unweathered sample may be employed. The following three paragraphs, together with the procedure below, describe displacement by self-induced pressure.

Maintain the sample container at a temperature sufficiently high to maintain superatmospheric pressure but not substantially over 100°F.

Completely immerse the gasoline chamber, with both valves open, in the cooling bath for a sufficient length of time to allow it to reach the bath temperature (32 to 40°F.).

Connect a suitable ice-cooled coil to the outlet valve of the sample container.

NOTE.—A suitable ice-cooled coil can be prepared by immersing a spiral of approximately 25 ft. of  $\frac{1}{4}$ -in. copper tubing in a bucket of ice water.

*Procedure.*—The earlier directions for sample transfer and assembly of apparatus on p. 1957 do not apply.

Connect the  $\frac{1}{4}$ -in. valve of the chilled gasoline chamber to the ice-cooled coil. With the  $\frac{1}{2}$ -in. valve of the gasoline chamber closed, open the outlet valve of the sample container and the  $\frac{1}{4}$ -in. valve of the gasoline chamber. Open the gasoline chamber  $\frac{1}{2}$ -in. valve slightly and allow the gasoline chamber to fill slowly. Allow the sample to overflow until the overflow volume is 200 ml. or more. Control this operation so that no appreciable drop in pressure occurs at the gasoline chamber  $\frac{1}{4}$ -in. valve. In the order named, close the gasoline chamber  $\frac{1}{2}$ -in. and  $\frac{1}{4}$ -in. valves; and then close all other valves in the sample system. Disconnect the gasoline chamber and the cooling coil. (*Caution:* Safe means for disposal of liquid and vapor escaping during this whole operation must be provided. To avoid rupture because of the liquid-full condition of the gasoline chamber, the gasoline chamber must be quickly attached to the air chamber and the  $\frac{1}{2}$ -in. valve opened.)

Immediately attach the gasoline chamber to the air chamber and open the gasoline chamber  $\frac{1}{2}$ -in. valve. Not more than 25 seconds shall be consumed in completing the assembly of the apparatus after filling the gasoline chamber, using the following sequence of operations: (1) read the initial air temperature or remove the air chamber from the water bath, (2) connect the air chamber to the gasoline chamber, and (3) open the gasoline chamber  $\frac{1}{2}$ -in. valve.

If a dead-weight tester is used instead of the mercury manometer, apply the calibration factor in pounds per square inch established for the pressure gage at or near the "uncorrected vapor pressure" to the "uncorrected vapor pressure," recording the value found as the "calibrated gage reading" to be used in the calculations of p. 1959 and Table 40-16 in place of the "manometer reading."

*Precautions.*—The precaution section on air saturation of sample (p. 1959) does not apply.

## MODIFICATIONS FOR AVIATION GASOLINE OF ABOUT 7 POUND VAPOR PRESSURE

The following paragraphs define changes in apparatus and procedure for the determination of the vapor pressure of aviation gasoline. Except as specifically stated herein, all the requirements set forth above should apply.

**Ratio of Air and Gasoline Chambers**—The ratio of the volume of the air chamber to the volume of the gasoline chamber should be between the limits of 3.9 and 4.05

**Water Cooling Bath**—The water cooling bath should be held at a temperature of 32 to 34°F

**Checking the Pressure Gage**—The gage should be checked at 7 lb against a mercury column before each vapor pressure measurement to insure that it conforms to the requirements of section on Pressure Gage p 1955 This preliminary check shall be made in addition to the final gage comparison specified under measurement of vapor pressure (p 1958)

**Air Chamber Temperature**—The provisions of Preparation of Air Chamber (100°F Procedure) apply (p 1956)

**Precision**—The following shall be used as a basis for judging the acceptability of results (95% probability)

**Repeatability**—Duplicate results by the same operators should not be considered suspect unless they differ by more than the amounts specified

Range	Repeatability (Same Operator and Apparatus)
0 to 5 lb	0.1
5 to 16 lb (except aviation gasoline)	0.2
16 to 26 lb	0.3
Above 26 lb	0.4
Aviation gasoline (approximately 7 lb)	0.1

**Reproducibility**—The results submitted by each of two laboratories should not be considered suspect unless they differ by more than the amounts specified

Range	Reproducibility (Different Operator and Apparatus)
0 to 5 lb	0.35
5 to 16 lb (except aviation gasoline)	0.3
16 to 26 lb	0.4
Above 26 lb	0.7
Aviation gasoline (approximately 7 lb)	0.15

CLOUD AND POUR POINTS <sup>15</sup>

The test for cloud point is intended for use only on oils which are transparent in layers  $1\frac{1}{2}$  in. in thickness.

The test for pour point is intended for use on any petroleum oil.<sup>15a</sup>

**Definitions.** **Cloud Point.**—The cloud point of a petroleum oil is the temperature at which paraffin wax or other solid substances begin to crystallize out or separate from solution when the oil is chilled under definite prescribed conditions.

**Pour Point.**—The pour point of a petroleum oil is the lowest temperature at which the oil will pour or flow when it is chilled without disturbance under definite prescribed conditions.

**Apparatus.**—The following apparatus shown in Fig. 40-20 should be used:

**Test Jar.**—A test jar, *a*, of clear glass, cylindrical form, flat bottom, approximately  $1\frac{3}{16}$  to  $1\frac{5}{16}$  in. in inside diameter and  $4\frac{1}{2}$  to 5 in. in height. An ordinary 4-oz. oil sample bottle may be used if it meets these requirements, and no test jar is available.

**Thermometer.**—An ASTM Cloud and Pour Test Thermometer having a range of  $-38$  to  $+50^{\circ}\text{C}$ . or  $-36$  to  $+120^{\circ}\text{F}$ ., as specified, and conforming to the requirements for thermometer 5C or 5F, respectively, as prescribed in ASTM Specifications E1,<sup>16</sup> or an ASTM Low Cloud and Pour Thermometer having a range of  $-80$  to  $+20^{\circ}\text{C}$ . or  $-112$  to  $+70^{\circ}\text{F}$ ., as specified, and conforming to the requirements for thermometer 6C or 6F, respectively as prescribed in Specifications E1.

**Coik.**—A coik, *c*, to fit the test jar, bored centrally to take the test thermometer.

**Jacket.**—A jacket, *d*, of glass or metal, water tight, of cylindrical form, flat bot-

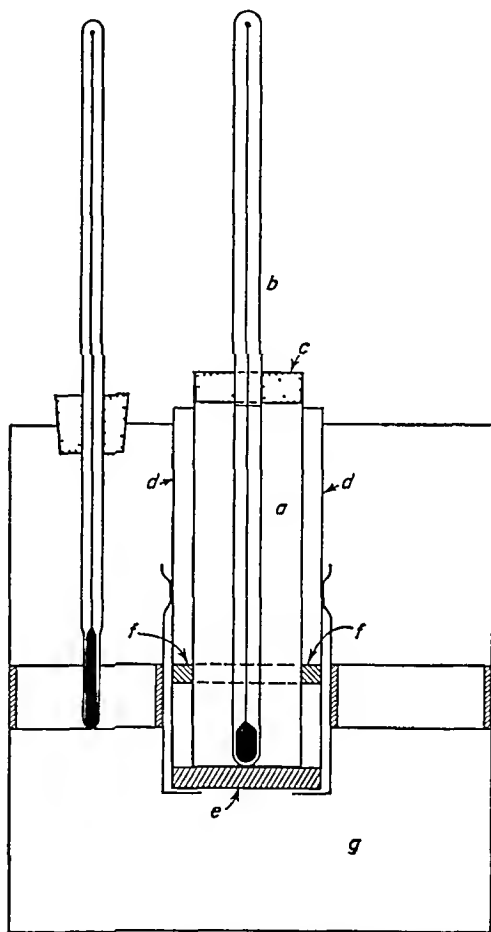


FIG. 40-20. Apparatus for Cloud and Pour Test, As Assembled for Cloud Test.

<sup>15</sup> Standardized as ASTM D97-57 and ASA No.: Z11 5-1957.

<sup>15a</sup> Statements defining this test and its significance when applied to electrical insulating oils of mineral origin will be found in ASTM Methods D117, Testing Electrical Insulating Oils

<sup>16</sup> For tests above  $-65^{\circ}\text{F}$ ., it is permissible to use the ASTM Low Cloud and Pour Thermometers having ranges of  $-60$  to  $+20^{\circ}\text{C}$ . and  $-70$  to  $+70^{\circ}\text{F}$ ., as previously prescribed for thermometers 6C-39 and 6F-39 in the Standard Specifications for ASTM Thermometers E1-46, 1946 Book of ASTM Standards, Part III-A, p. 718.

tom about  $4\frac{1}{2}$  in in depth with inside diameter  $\frac{3}{8}$  to  $\frac{1}{2}$  in greater than the outside diameter of the test jar

Disk—A disk of cork or felt *e*  $\frac{1}{4}$  in in thickness and of the same diameter as the inside of the jacket

Gasket A ring gasket *f* about  $\frac{3}{16}$  in in thickness to fit snugly around the outside of the test jar and loosely inside the jacket This gasket may be made of cork felt or other suitable material elastic enough to cling to the test jar and hard enough to hold its shape The purpose of the ring gasket is to prevent the test jar from touching the jacket

Bath—A cooling bath *g* of a type suitable for obtaining the required temperatures The size and shape of the bath are optional but a support suitable for holding the jacket firmly in a vertical position is essential For determinations of pour points below 50°F two or more baths should be at hand The required bath temperatures may be maintained by refrigeration if available otherwise by suitable freezing mixtures

NOTE—The freezing mixtures commonly used are as follows

	<i>For Temperatures Down To</i>
Ice and water	50°F
Crushed ice and sodium chloride	10°F
Crushed ice and calcium chloride crystals	-15°F
Solid carbon dioxide and acetone or gasoline *	-70°F

\* This mixture may be made as follows In a covered metal beaker chill a suitable amount of acetone or gasoline to 10°F or lower by means of an ice salt mixture Invert a cylinder of liquid carbon dioxide and draw off carefully into a chamois skin bag the desired amount of carbon dioxide which through rapid evaporation will quickly become solid Then add to the chilled acetone or gasoline enough of the solid carbon dioxide to give the desired temperature

*Procedure for Cloud Point* Bring the oil to be tested to a temperature at least 20°F above the approximate cloud point Remove moisture if present by any suitable method as by filtration through dry lintless filter paper until the oil is perfectly clear but make such filtration at a temperature at least 20°F above the approximate cloud point

Pour the clear oil into the test jar *a* to a height of not less than 2 nor more than  $2\frac{1}{4}$  in Mark the test jar to indicate the proper level

Tightly close the test jar by the cork *c* carrying the test thermometer *b* in a vertical position in the center of the jar with the thermometer bulb resting on the bottom of the jar

Place the disk *e* in the bottom of the jacket *d* and insert the test jar with the ring gasket *f* 1 in above the bottom into the jacket The disk gasket and inside of jacket shall be clean and dry

Maintain the temperature of the cooling bath *g* at 30 to 35°F Support the jacket containing the test jar firmly in a vertical position in the cooling bath so that not more than 1 in of the jacket projects out of the cooling medium

At each test thermometer reading that is a multiple of 2°F remove the test jar from the jacket quickly but without disturbing the oil inspect for cloud and

replace in the jacket. This complete operation shall require not more than 3 seconds. If the oil does not show a cloud when it has been cooled to 50°F., place the test jar in the jacket in a second bath maintained at a temperature of 0 to +5°F. If the oil does not show a cloud when it has been cooled to 20°F., place the test jar in the jacket in a third bath maintained at a temperature of -30 to -25°F.

When such inspection first reveals a distinct cloudiness or haze in the oil at the bottom of the test jar, record the reading of the test thermometer, corrected for error if necessary, as the cloud point.

NOTE.—A wax cloud or haze is always noted first at the bottom of the test jar where the temperature is lowest. A slight haze throughout the entire sample, which slowly becomes more apparent as the temperature is lowered, is usually due to traces of water in the oil. Generally, this water haze will not interfere with the determination of the wax cloud point. In most cases of interference, filtration through dry lintless filter papers is sufficient.

In the case of diesel fuels, however, if the haze is very dense, a fresh portion of the sample should be dried by shaking 100 ml. with 5 g. of anhydrous sodium sulfate for at least 5 minutes and then filtering through dry lintless filter paper. Given sufficient contact time, this will remove or sufficiently reduce the water haze so that the wax cloud can be readily discerned. Drying and filtering should be done always at a temperature at least 25°F. above the approximate cloud point but otherwise not in excess of 120°F. Remove moisture, if present, by any suitable method, as by filtration through dry lintless filter paper until the oil is perfectly clear, but make such filtration at a temperature at least 25°F. above the approximate cloud point.

*Procedure for Pour Point.*—Pour the oil into the test jar, *a*, to a height of not less than 2 nor more than 2¼ in. Mark the jar to indicate the proper level. When necessary, heat the oil in a water bath just sufficiently for pouring into the test jar.

Close the test jar tightly by the cork, *c*, carrying the test thermometer, *b*, in a vertical position in the center of the jar with the thermometer bulb immersed so that the beginning of the capillary shall be ⅓ in. below the surface of the oil.

Heat the oil, without stirring, to a temperature of 115°F. in a bath maintained at not higher than 118°F. Cool the oil to 90°F. in air or in a water bath approximately 77°F. in temperature. Heat oils on which a pour point below -30°F. is expected as above with the high cloud- and pour-test thermometer in position, cool to 60°F., place the low cloud- and pour-test thermometer in position, and then place the assembly in the jacket. Heat oils on which a pour point of above 90°F. is expected to 115°F. or to a temperature 15°F. above the expected pour point, with the high cloud- and the pour-test thermometer in position, and immediately introduce the test jar into the jacket.

Place the disk, *e*, in the bottom of the jacket, *d*, and insert the test jar, with the ring gasket, *f*, 1 in. above the bottom, into the jacket. The disk, gasket and inside of jacket should be clean and dry.

After the oil has cooled enough to allow the formation of paraffin wax crystals, take great care not to disturb the mass of the oil nor to permit the thermometer to shift in the oil. Any disturbance of the spongy network of wax crystals will lead to low and fictitious results.

Maintain the temperature of the cooling bath, *g*, at 30 to 35°F. Support the jacket, containing the test jar, firmly in a vertical position in the cooling bath so that not more than 1 in. of the jacket projects out of the cooling medium.

Beginning at a temperature 20°F. before the expected pour point, at each test

thermometer reading that is a multiple of 5°F remove the test jar from the jacket carefully and tilt it just enough to ascertain whether there is a movement of the oil in the test jar. The complete operation of removal and replacement shall require not more than 3 seconds. If the oil has not ceased to flow when its temperature has reached 50°F place the test jar in the jacket in a second bath maintained at a temperature of 0 to +5 F. If the oil has not ceased to flow when its temperature has reached 20°F place the test jar in the jacket in a third bath maintained at a temperature of -30 to -25°F. For determinations of very low pour points additional baths should be maintained with successively lower temperature differentials of about 30°F. In each case transfer the test jar when the temperature of the oil reaches a point 50°F above the temperature of the new bath. At no time place the cold test jar directly in the cooling medium. As soon as the oil in the test jar does not flow when the jar is tilted hold the test jar in a horizontal position for exactly 5 seconds as noted by a stop watch or other accurate timing device and observe carefully. If the oil shows any movement under these conditions replace the test jar immediately in the jacket and repeat a test for flow at the next temperature 5°F lower.

Continue the test in this manner until a point is reached at which the oil in the test jar shows no movement when the test jar is held in a horizontal position for exactly 5 seconds. Certain lubricating oils tend to move as a whole and should be very closely observed. Record the reading of the test thermometer at this temperature corrected for error if necessary. Take the pour point as the temperature 5°F above this solid point.

### SPECIAL PROCEDURE FOR BLACK OILS, CYLINDER STOCKS AND NONDISTILLATE FUEL OILS

*Special Procedure for Pour Point*—In those cases where it is known that a sample has been subjected to some temperature higher than 115°F during the preceding 24 hours or where the history of the sample in this respect is not known hold the sample in the laboratory 24 hours before testing unless three consecutive tests in accordance with the six paragraphs preceding which start with the words

Heat the oil without stirring of the same sample in the same test jar give check results. For these particular oils results obtained by one or the other of the alternative procedures shall be called the upper (maximum) pour point.

Determine the lower (minimum) pour point by heating a sample while stirring to 220°F. Then pour the oil into the test jar cooled to 90°F as before and determine the pour point as described in preceding section.

Report both the upper and lower pour points.

*Reproducibility of Results*—Individual results of the pour test on the same oil in any one laboratory may vary by 5°F and in different laboratories by 10°F although the average of three or more results in different laboratories should show a difference between averages no greater than 5°F. For oils tested by the special procedure described in the preceding section reproducibility of this order cannot be expected, as these oils show anomalous pour points depending on their previous thermal history.<sup>16a</sup>

<sup>16a</sup> It is a recognized property of these oils that the temperature to which they have been subjected before testing influences their pour points. Although the lower pour points as determined by the special procedure will show approximately the reproducibility given

EXISTENT GUM IN FUELS BY JET EVAPORATION <sup>17</sup>

This method describes a procedure for determining the gum existent in motor gasoline and aircraft fuels at the time of test.

**Definition.** Existent Gum is the evaporation residue of aircraft fuel or the heptane-insoluble portion of the evaporation residue of motor gasoline.

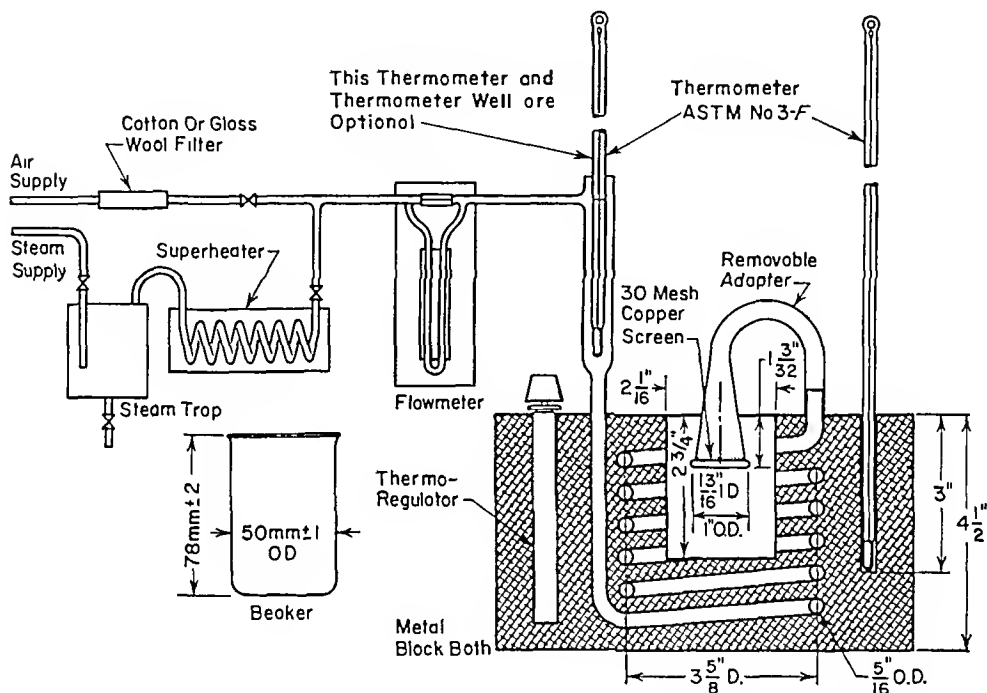


FIG. 40-21. Apparatus for Determining Existent Gum by Jet Evaporation.

**Outline of Method.**—A measured quantity of fuel is evaporated under controlled conditions of temperature and flow of air or steam. For aviation gasoline and aircraft turbine fuel, the resulting residue is weighed and reported as milligrams per 100 ml. For motor gasoline, the residue is extracted with heptane, dried, weighed, and reported as milligrams per 100 ml.

**Apparatus.** Evaporation Bath.—Either a solid metal block bath or liquid bath, electrically heated, and constructed in accordance with the general principles shown in Fig. 40-21 shall be used. The bath should have wells and jets for two or more beakers. The rate of flow from each outlet when fitted with the conical adapters should not differ from 1000 ml. per second by more than 15%. A liquid bath,

above, yet the upper pour points will show greater variations depending on the previous thermal history of the oils. Further information on this subject is contained in *Proceedings*, Am. Soc. Testing Mats., Vol. 31, Part I, pp. 468 to 470 (1931), and Vol. 32, Part I, pp. 402 to 405 (1932).

<sup>17</sup> Approved as ASTM D381-61R and ASA No.: Z11.36-1961.

if used shall be filled to within 1 in. of the top with a suitable liquid. Temperature may be maintained by means of thermostatic controls or by refluxing liquids of suitable composition.

Flowmeter, capable of metering a flow of air or steam equivalent to 1000 ml per second for each outlet.

Steam Superheater, gas fired or electrically heated, capable of delivering to the bath inlet the required amount of steam at 450°F (232°C).

Beakers of 100 ml capacity as illustrated in Fig. 40.21. Arrange the beakers in sets, the number in each set depending upon the number of beaker wells in the evaporating bath. Permanently mark each beaker in the set with an identifying number or letter, reserving the lowest weight beaker for use as a tare.

Cooling Vessel—A desiccator or other type of tightly covered vessel for cooling the beakers before weighing. The use of a drying agent is not recommended.

Balance, having a sensitivity of 0.5 mg per scale division or better.

Thermometer, ASTM Partial Immersion, having a range of 20 to 760 F or -20 to +400 C as specified and conforming to the requirements for thermometer 3F or 3C respectively as prescribed in ASTM Specifications E1.

Sintered Glass Filtering Funnel,<sup>18</sup> coarse porosity, 150 ml capacity.

Materials—Air—Supply of filtered air at a pressure not more than 5 psi.

Steam—Supply of steam free of oily residue and at a pressure not less than 5 psi.

Gum Solvent—A mixture of equal volumes of benzene and acetone.

Heptane, ASTM knock test grade conforming to the requirements given in Table 40.17.

TABLE 40.17 REQUIREMENTS FOR *n* HEPTANE

ASTM Motor Octane Number <sup>a</sup>	00 ± 0.2
Density at 20°C, <sup>b</sup> g per ml	0.68380 ± 0.00015
Refractive Index, <sup>c</sup> $n_D^{20}$	1.38770 ± 0.00015
Freezing Point, <sup>d</sup> deg. Cent	-90.710 min
Distillation <sup>e</sup>	
50% Recovered, deg. Cent (at 760 mm. of Hg)	98.427 ± 0.025
Differential, 80% Recovered minus 20% Recovered, deg. Cent	0.020 max

<sup>a</sup> Determined in accordance with ASTM Method D357, Test for Knock Characteristics of Motor Fuels Below 100 Octane Number by the Motor Method.

<sup>b</sup> Determined in accordance with ASTM Method D217, Test for Density and Specific Gravity of Liquids by Bingham Pycnometer.

<sup>c</sup> Determined in accordance with ASTM Method D1218, Measurement of Refractive Index and Refractive Dispersion of Hydrocarbon Liquids.

<sup>d</sup> Determined in accordance with ASTM Method D1015, Test for Freezing Points of High Purity Hydrocarbons.

<sup>e</sup> For equipment and method used see *Journal of Research*, Nat. Bureau Standards 44, No. 3, 1950, pp. 309 and 310 (RP2079).

<sup>18</sup> A Corning No. 36060 sintered glass filtering funnel has been found satisfactory for this purpose.



NOTE.—These requirements for *n*-heptane are identical, except for tetraethyl lead, with those prescribed in the 1961 Supplement to the ASTM Manuals for Engine Ratings of Fuels.<sup>19</sup>

**Assembly of Air-Jet Apparatus.**—Assemble the air-jet apparatus as shown in Fig. 40-21. With the apparatus at room temperature, adjust the air flow to give a rate of 600 ml. per second for the outlet under test. Check the remaining outlets for uniform air flow. Make necessary changes to individual outlets if the rate differs by more than  $600 \pm 90$  ml. per second.

NOTE.—A flowmeter reading of 600 ml. per sec. for each outlet on a flowmeter calibrated at room temperature and atmospheric pressure will insure delivery of  $1000 \pm 150$  ml. per second at the temperature of  $311 \pm 9^\circ\text{F.}$  ( $155 \pm 5^\circ\text{C.}$ ), provided the pressure on the outlet of the flowmeter is not greater than 5 psi.

To place the apparatus in operation, apply heat to the bath. When the temperature reaches  $324^\circ\text{F.}$  ( $162^\circ\text{C.}$ ), introduce air into the apparatus until a rate of  $1000 \pm 150$  ml. per second for each outlet is reached. Measure the temperature in each well with an ASTM Thermometer 3F or 3C placed with the bulb resting on the bottom of the beaker in the well. Any well having a temperature that differs by more than  $9^\circ\text{F.}$  ( $5^\circ\text{C.}$ ) from  $311^\circ\text{F.}$  ( $155^\circ\text{C.}$ ) is not suitable for standard tests.

**Assembly of Steam-Jet Apparatus.**—Assemble the steam-jet apparatus as shown in Fig. 40-21.

To place the apparatus in operation, apply heat to the bath. When the temperature reaches  $450^\circ\text{F.}$  ( $232^\circ\text{C.}$ ), apply heat to the superheater and slowly introduce dry steam into the system until a rate of  $1000 \pm 150$  ml. per second for each outlet is reached. Regulate the temperature of the bath to a range of  $450$  to  $475^\circ\text{F.}$  ( $232$  to  $246^\circ\text{C.}$ ) and the superheater to provide a well temperature of  $450 \pm 5^\circ\text{F.}$  ( $232 \pm 2.8^\circ\text{C.}$ ). Measure the temperature with an ASTM Thermometer 3F or 3C, placed with the bulb resting on the bottom of a glass sample container in one of the bath wells with the conical adapter in place. Any well having a temperature that differs by more than  $5^\circ\text{F.}$  ( $2.8^\circ\text{C.}$ ) from  $450^\circ\text{F.}$  ( $232^\circ\text{C.}$ ) is not suitable for standard tests.

Calibrate the flowmeter by successively condensing the steam flow from each outlet and weighing the water condensate. To accomplish this, attach a copper tube to a steam outlet and extend the tube into a 2-l. graduate that has been filled with crushed ice and then weighed. Exhaust the steam into the graduate for approximately 60 seconds. Adjust the position of the graduate so that the end of the copper tube is immersed in the water to a depth of less than 2 in. to prevent excessive back pressure. Weigh the graduate. The gain in weight represents the amount of steam condensed. Calculate the steam rate as follows:

$$R = \frac{(W - w)1000}{kt}$$

where  $R$  = steam rate, milliliters of steam at  $450^\circ\text{F.}$  ( $232^\circ\text{C.}$ ) per sec.,

$W$  = weight of graduate with condensed steam, in grams,

$w$  = weight of graduate and ice, in grams,

$k$  = weight of 1000 ml. of steam at  $450^\circ\text{F.}$  ( $232^\circ\text{C.}$ ) at atmospheric pressure = 0.434 g., and

$t$  = condensing time, in seconds.

<sup>19</sup> Issued as a separate publication.

## 1970 PETROLEUM AND PETROLEUM PRODUCTS

Adjust the flow to give a steam rate of 1000 ml per second for the outlet under test. Check the remaining outlets for uniform steam flow. Make necessary changes to individual outlets if the rate varies by more than 150 ml of steam per second. With all outlets adjusted to deliver  $1000 \pm 150$  ml of steam per second, record the flowmeter reading and use this setting for subsequent testing.

**Procedure**—Wash the beakers (including the tire) with the gum solvent until free of gum. Rinse thoroughly with water and immerse for at least 6 hours in chromic acid cleaning solution. Remove the beakers from the cleaning solution by means of stainless steel forceps and handle only with forceps thereafter. Wash the beakers thoroughly first with tap water and then with distilled water and dry in an oven at 302°F (150°C) for at least 1 hour. Cool the beakers for at least 2 hours in the cooling vessel placed in the vicinity of the balance.

Select the operating conditions corresponding to the motor gasoline or aviation fuel under test from the data given in Table 40.18. Heat the bath to the pre-

TABLE 40.18 SCHEDULE OF TEST CONDITIONS

Sample Type	Vaporizing Medium	Operating Temperature	
		Bath	Test Well
Aviation and motor gasoline	Air	320 to 329°F (160 to 165°C)	302 to 320°F (150 to 160°C)
Aircraft turbine fuel	Steam	450 to 475°F (232 to 246°C)	445 to 455°F (229 to 235°C)

scribed operating temperature. Introduce air or steam to the apparatus and adjust the flow to  $1000 \pm 150$  ml per second. If an external preheater is used, regulate the temperature of the vaporizing medium to give the prescribed test well temperature.

Place the tare beaker on the right hand pan of the balance and weigh the test beakers to the nearest 0.1 mg. When a single pan type balance is used, weigh the tare beaker as a blank. Record the weights.

If suspended or settled solid matter is present, mix the contents of the container thoroughly. Immediately filter at atmospheric pressure a quantity of the fuel through a sintered glass funnel of coarse porosity. Treat the filtrate as described below.

By means of graduates, add 50 ml of fuel to each beaker except the tare, using one beaker for each of the fuels to be tested. Place the filled beakers (including the tare) in the evaporation bath. The elapsed time between placing the first and last beaker in the bath must be as short as possible. When evaporating fuels by means of air, replace the conical jet as each individual beaker is placed in the bath. When using steam, allow the beakers to heat for 3 minutes before replacing the conical jet, which must be preheated in the steam stream prior to attachment to the outlets. Center the jets above the surface of the liquid. Maintain the

temperature and rate of flow and allow the fuel to evaporate for 30 minutes. Samples tested simultaneously should have equal evaporation characteristics.

At the end of the heating period, remove the beakers from the bath and allow them to cool to room temperature. Segregate the beakers containing the residues from motor gasolines for finishing as described in the second, third, and fourth paragraphs following. Treat the remaining beakers as described in the following paragraph.

Place the beakers containing the residues from aviation gasolines and aircraft turbine fuels in the cooling vessel in the vicinity of the balance for at least 2 hours. Weigh the beakers in the same manner as described in the paragraph above, beginning "Place the tare beaker . . ." Record the weights. Calculate the existent gum as described in the section below headed "Calculation."

To each of the beakers containing the residues from motor gasolines segregated as directed in the above paragraph beginning "At the end of the heating period . . .", add 25 ml. of *n*-heptane and swirl gently for 30 seconds. Allow the mixture to stand for 10 minutes. Treat the tare beaker in the same manner.

Decant and discard the heptane solution, taking precaution to prevent the loss of any solid residue.

Repeat the extraction with a second 25-ml. portion of *n*-heptane as described in the preceding two paragraphs. Repeat the extraction a third time, if the extract is colored.

Place the beakers, including the tare, in the gum bath maintained at 320 to 329°F. (160 to 165°C.) and, without replacing the conical jets, allow the beakers to dry for 5 minutes.

At the end of the drying period, remove the beakers from the bath, place them in a cooling vessel, and allow to cool in the vicinity of the balance for at least 2 hours. Weigh the beakers in the same manner as described in the earlier paragraph beginning, "Place the tare beaker . . ." Record the weights. Calculate the existent gum as described below.

Calculation.—If a double-pan balance is used, calculate the existent gum content as follows:

$$A = 2000(B - C)$$

where  $A$  = existent gum content, milligrams per 100 ml.,

$B$  = weight of sample beaker plus existent gum, in grams, and

$C$  = weight of empty sample beaker, in grams.

If a single-pan balance is used, calculate the existent gum content as follows:

$$A = 2000(B - C + X - Y)$$

where  $A$  = existent gum content, milligrams per 100 ml.,

$B$  = uncorrected weight of sample, beaker plus existent gum, in grams,

$C$  = weight of empty sample beaker, in grams,

$X$  = original weight of tare beaker, in grams, and

$Y$  = final weight of tare beaker, in grams.

Report.—Report the existent gum values, to the nearest milligram per 100 ml.

After the numerical value for existent gum, designate by the word "filtered" the fact that extraneous material has been removed as provided for in the earlier paragraph beginning, "If suspended or settled solid . . .".

**Precision**—Two determinations on the same sample should not differ from each other by more than the amounts shown in Fig 40 22

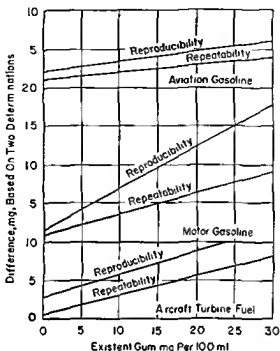


FIG 40 22 Precision

## WATER IN PETROLEUM PRODUCTS AND OTHER BITUMINOUS MATERIALS <sup>19a</sup>

This method of test is used to determine the water content of bituminous materials by distillation with a water immiscible, volatile solvent. The method is suitable for a variety of bituminous materials, but it is especially applicable to crude petroleum and tars and products derived from them, such as fuel oils, road oils, creosotes, road tars, and asphalts.

**Outline of Method**—The material is heated under reflux with a water immiscible solvent which co-distills with the water in the sample. Condensed solvent and water are continuously separated in a trap, the water settling in the graduated section of the trap and the solvent returning to the still.

**Apparatus** <sup>20</sup>—The apparatus comprises a glass or metal still, a heater, a reflux condenser, and a graduated glass trap. The still, trap, and condenser may be connected by any suitable method for producing a leak proof joint. Preferred connections are ground joints for glass to glass and O rings for metal to glass. Typical assemblies are illustrated in Figs 40 23 and 40 24.

**Still**—A glass or metal vessel having a nominal capacity of 500 to 1000 ml and a short neck accommodating the reflux tube of the trap.

<sup>19a</sup> Standardized as ASTM D95 58 and ASA No. Z11.9 1956

<sup>20</sup> Constructional details of the apparatus are prescribed in ASTM Specifications E123, for Apparatus for Determination of Water by Distillation.

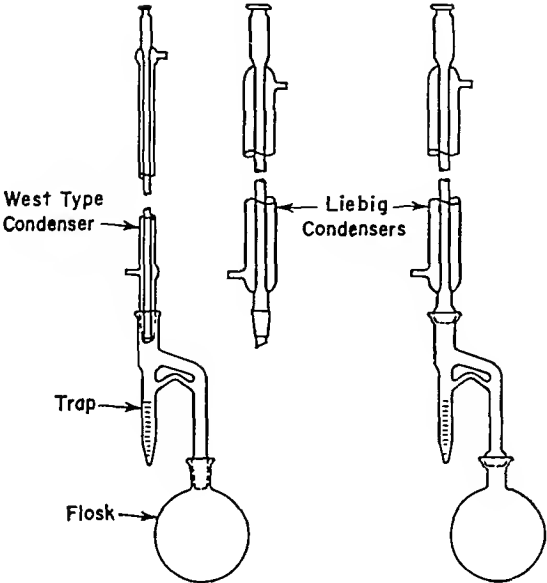


FIG. 40-23. Typical Assemblies with Glass Flask; Trap Should Be Set 15 to 16 mm. I.D.

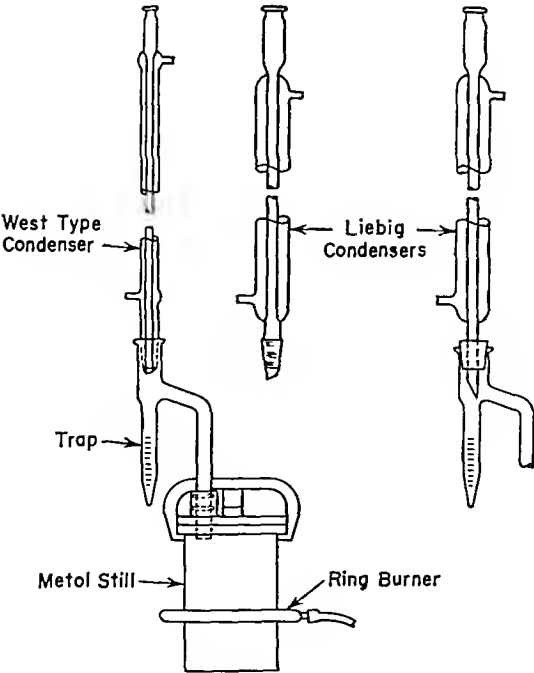


FIG. 40-24. Typical Assemblies with Metal Still; Trap Should Be 15 to 16 mm. I.D.

**Heater**—Any suitable gas burner or electric heater may be used with the glass flask. A gas ring burner with ports on the inside circumference shall be used with the metal still.

**Condenser**—A straight tube condenser having a jacket at least 400 mm long and an inner tube whose outside diameter is 9.5 to 12.7 mm.

**Trap**—A glass trap of 10 or 25 ml capacity. The traps shall be graduated in 0.1 ml divisions with a  $\pm 0.05$  ml maximum error below 1 ml and in 0.2 ml divisions with a  $\pm 0.1$  ml maximum error above 1 ml.

**Solvent**—For general use an aromatic solvent is preferred since it has high solvency and dispersing power for most bituminous materials. Xylol or a blend of 20% benzol and 80% xylol is recommended.

For asphalts and similar petroleum products a petroleum distillate 5% boiling between 194 and 212°F and 90% distilling below 410 F may be used.

For coal tar, water gas tar and similar materials the aromatic solvent must be used.

**Sample** The portion of the sample used for the test must be thoroughly representative of the total sample. If the material is liquid thoroughly stir the sample is received warming if necessary to insure uniformity. Crush the solid materials that are sufficiently brittle mix thoroughly and take a representative sample for analysis. When there is doubt as to the uniformity of the material run a number of samples and average the data.

Base the size of the test portion on the estimated water content of the sample such that the water yield does not exceed the capacity of the trap.

**Procedure**—Transfer a suitable amount of sample measured with an accuracy of  $\pm 1\%$  to the still. Measure ordinary liquid samples in a graduated cylinder of appropriate size. Rinse the material adhering to the cylinder into the still with one 50 ml and two 25 ml portions of the solvent. Drain the cylinder thoroughly after the sample transfer and each rinsing. Weigh solid or semi-solid materials or bituminous emulsions directly into the still and add 100 ml of solvent. When large samples are being analyzed a solvent volume in excess of 100 ml may be necessary.

Assemble the components of the apparatus as illustrated in Figs. 40-23 and 40-24 making all connections vapor and liquid tight. If a metal still with removable cover is used insert a gasket of heavy paper moistened with solvent between the still body and cover. The condenser tube and trap must be chemically clean to assure free drainage of water into the bottom of the trap. Insert a loose cotton plug at the top of the condenser to prevent condensation of atmospheric moisture inside it. Circulate cold water through the jacket of the condenser.

Apply heat to the still adjusting the rate of boiling so that condensed distillate discharges from the condenser at the rate of 2 to 5 drops per second. If the metal still is used start heating with the ring burner about 3 in. above the bottom of the still and gradually lower the burner as the distillation proceeds. Continue distillation until no water is visible in any part of the apparatus except in the trap. If there is a persistent ring of water in the condenser tube increase the rate of distillation or cut off the condenser water for a few minutes.

When the evolution of water is completed allow the trap and contents to cool to room temperature. Dislodge any drops of water adhering to the sides of the trap with a glass or polytetrafluoroethylene or other suitable means and transfer them to the water layer. Read the volume of the water in the trap to the nearest scale division.

Report.—Report the water in the sample as per cent by weight or volume, according to the basis on which the sample was taken, calculated as follows:

$$\text{Water, \%} = \frac{\text{vol. of water in trap}}{\text{wt. (or vol.) of sample}} \times 100$$

Volatile water-soluble material present may also be measured as water.

**Precision.**—Two tests of the same material should agree within the greater of the following limits:

<i>Volume of Water Collected, ml.</i>	<i>Repeatability (Same Appa- ratus and Operator)</i>	<i>Reproducibility (Different Ap- paratus and Operator)</i>
0 to 1.....	0.1 ml.	0.2 ml.
Over 1 to 25.....	0.1 ml. or $\pm 1\%$ of the mean	0.2 ml. or $\pm 5\%$ of the mean

## WATER AND SEDIMENT IN FUEL OILS BY CENTRIFUGE <sup>21</sup>

This method describes a procedure for the determination of water and sediment in fuel oils and related petroleum products by means of the centrifuge.

**NOTE.**—With some types of fuels, especially residual fuels, it is difficult to obtain an accurate water and sediment content in accordance with this method, due to suspended carbon or other materials. When this situation is encountered, ASTM Method D95, Test for Water in Petroleum Products and Other Bituminous Materials, and ASTM Method D473, Test for Sediment in Fuel Oil by Extraction, may be used.

**Apparatus.** Centrifuge, capable of whirling two or more filled centrifuge tubes at a speed which can be controlled to give a relative centrifugal force (r.c.f.) of between 500 and 800 at the tip of the tubes. The revolving head, trunnion rings and trunnion cups, including the cushions, shall be soundly constructed to withstand the maximum centrifugal force capable of being delivered by the power source. The trunnion cups and cushions shall firmly support the tubes when the centrifuge is in motion. The centrifuge shall be enclosed by a metal shield or case strong enough to eliminate danger if any breakage occurs. Calculate the speed of the rotating head as follows:

$$\text{r.p.m.} = 265 \sqrt{\frac{\text{r.c.f.}}{d}}$$

where r.c.f. = relative centrifugal force, and

$d$  = diameter of swing, in inches, measured between tips of opposite tubes when in rotating position.

**Centrifuge Tube**, cone-shaped, conforming to dimensions given in Fig. 40-25 and made of thoroughly annealed glass. The graduations, numbered as shown in Fig. 40-25, shall be clear and distinct, and the mouth constricted in shape for closure with a cork. Scale error tolerances and smallest graduations between various calibration marks are given in Table 40-19, and apply to calibrations made with air-free water at 20°C. reading the bottom of a shaded meniscus.

<sup>21</sup> Approved as ASTM D1796-60T.

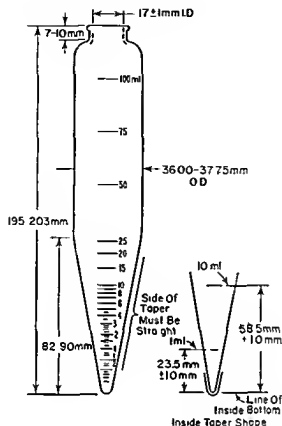


FIG 40 25 ASTM Centrifuge Tube For Volumetric Tolerances see Table 40 19

TABLE 40 19 CENTRIFUGE TUBE CALIBRATION TOLERANCES

Range, ml	Subdivision, ml	Volume Tolerance, ml
0 to 0.1	0.05	$\pm 0.02$
Above 0.1 to 0.3	0.05	$\pm 0.03$
Above 0.3 to 0.5	0.05	$\pm 0.05$
Above 0.5 to 1.0	0.10	$\pm 0.05$
Above 1.0 to 2.0	0.10	$\pm 0.10$
Above 2.0 to 3.0	0.20	$\pm 0.10$
Above 3.0 to 5.0	0.5	$\pm 0.20$
Above 5.0 to 10	1.0	$\pm 0.50$
Above 10 to 25	5.0	$\pm 1.00$
Above 25 to 100	25	$\pm 1.00$



**Bath.**—The bath shall be either a solid metal block bath or a liquid bath of sufficient depth for immersing the centrifuge tube in vertical position to the 100-ml. mark. Means shall be provided for maintaining temperatures at  $120 \pm 2^{\circ}\text{F.}$  ( $49 \pm 1^{\circ}\text{C.}$ ) and  $140 \pm 2^{\circ}\text{F.}$  ( $60 \pm 1^{\circ}\text{C.}$ ).

**Solvent.**—Toluene conforming to ASTM Specifications D842, for Industrial Grade Toluene; or Benzene, conforming to ASTM Specifications D836, for Industrial Grade Benzene, may be used as the solvent. A demulsifier <sup>21a</sup> shall be added to the solvent. The type and concentration is not limited, provided that the demulsifier itself does not contribute to the volume of water and sediment. The solvent shall be water saturated at ambient temperature, but shall be free of suspended water. This may be accomplished by the addition of 3 ml. of water per gallon of solvent. Shaking will aid in saturation, but adequate settling time is necessary to insure that the solvent is free of suspended water before use.

**NOTE.**—Toluene is the preferable solvent because of its lower toxicity.

**Sample.**—The sample shall be thoroughly representative of the material in question and the portion used for the test shall be thoroughly representative of the sample itself. This requires vigorous agitation of the sample before transferring the sample to the tube. Cold samples of heavy fuel oils should be warmed to facilitate mixing. The difficulties in obtaining representative samples for this determination are unusually great; hence, the importance of sampling cannot be too strongly emphasized.

**Procedure.**—Fill the centrifuge tube exactly to the 50-ml. mark with the solvent; then pour the well shaken sample directly from the sample container into the centrifuge tube until the total volume in the tube is exactly 100 ml. Read the top of the meniscus at both the 50- and 100-ml. marks. Stopper the tube tightly and shake vigorously until the contents are thoroughly mixed. Immerse the tube to the 100-ml. mark for 10 minutes in the bath maintained at  $120 \pm 2^{\circ}\text{F.}$  ( $49 \pm 1^{\circ}\text{C.}$ ).

**NOTE.**—If wax contributes to the volume of water and sediment observed, preheat the oil-solvent mixture to  $140^{\circ}\text{F.}$  ( $60^{\circ}\text{C.}$ ) before each whirling; the final temperature of the oil-benzene mixture should not drop below  $115^{\circ}\text{F.}$  ( $46^{\circ}\text{C.}$ ).

Shake the tube vigorously until thoroughly mixed, place in a trunnion cup opposite another filled tube to establish a balanced condition, and whirl 10 minutes at a rate, calculated from the equation given under Centrifuge (above), sufficient to produce a relative centrifugal force (r.c.f.) of between 500 and 800 at the tip of the whirling tubes (see Table 40-20 for the relationship between diameter of swing, r.c.f., and r.p.m.). Read and record the combined volume of water and sediment at the bottom of the tube to the nearest 0.05 ml. from 0.1- to 1-ml. graduation and to the nearest 0.1 above 1-ml. graduation. Below 0.1 ml., estimate to the nearest 0.025 ml. Return the tube to the centrifuge and whirl for 10 minutes at the same rate. Repeat this operation until the combined volume of water and sediment remains constant for two consecutive readings. In general, not more than two whirlings are required.

**NOTE.**—If the oil-water interface is not sharply defined or an emulsion phase is present, use a different or an increased amount of demulsifier.

<sup>21a</sup> Commercial crude oil demulsifiers, such as Tretolite F-46 and C-10 at a concentration of 25 ml. per gal. of solvent, have been successfully used.

TABLE 40-20 ROTATION SPEEDS APPLICABLE FOR CENTRIFUGES OF VARIOUS DIAMETERS OF SWING

Diameter of Swing, in *	Rpm at 500 rcf	Rpm at 800 rcf
12	1710	2160
13	1650	2080
14	1590	2000
15	1530	1930
16	1480	1870
17	1440	1820
18	1400	1770
19	1360	1720
20	1330	1680
21	1300	1640
22	1270	1600
23	1240	1560
24	1210	1530

\* Measured in inches between tips of opposite tubes when in rotating position

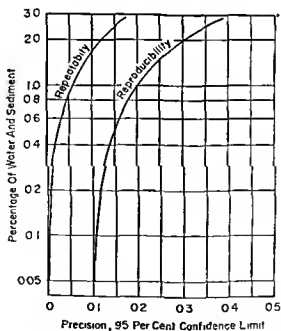


FIG 40-26 Precision Curves for Centrifuge Tube Methods

**Calculation and Report.**—Multiply the combined volume of water and sediment by two and record the product as the percentage of water and sediment. Report results lower than 0.05% either as zero or 0.05, whichever is closer.

Report the type and amount of demulsifier used.

**Precision.**—The following criteria should be used for judging the acceptability of results (95% probability):

**Repeatability.**—Duplicate results by the same operator should not be considered suspect unless they differ by more than the values shown on the "repeatability" curve in Fig. 40-26.

## ANILINE POINT AND MIXED ANILINE POINT OF PETROLEUM PRODUCTS AND HYDROCARBON SOLVENTS <sup>22</sup>

This method describes the test procedures for determining the aniline point of petroleum products and hydrocarbon solvents, provided the aniline point is below the bubble point and above the solidification point of the aniline-sample mixture.

*This method also provides a procedure for determining the mixed aniline point of petroleum products and hydrocarbon solvents having aniline points below the temperature at which aniline will crystallize from the aniline-sample mixture.*

**Definitions.** **Aniline Point** is the minimum equilibrium solution temperature for equal volumes of aniline and sample.

**Mixed Aniline Point** is the minimum equilibrium solution temperature of a mixture of two volumes of aniline, one volume of sample, and one volume of *n*-heptane of specified purity.

**Outline of Method.**—Specified volumes of aniline and sample or aniline and sample plus diluent are placed in a tube and mixed mechanically. The mixture is heated at a controlled rate until the two phases become miscible. The mixture is then cooled at a controlled rate and the temperature at which the two phases separate is recorded as the aniline point or mixed aniline point.

**Apparatus for Method I.**—The apparatus shown in Fig. 40-27 shall consist of the following:

**Test-Tube.**—A test-tube approximately 25 mm. in diameter and 150 mm. in length, made of heat-resistant glass.

**Jacket.**—A jacket approximately 37 to 42 mm. in diameter and 175 mm. in length, made of heat-resistant glass.

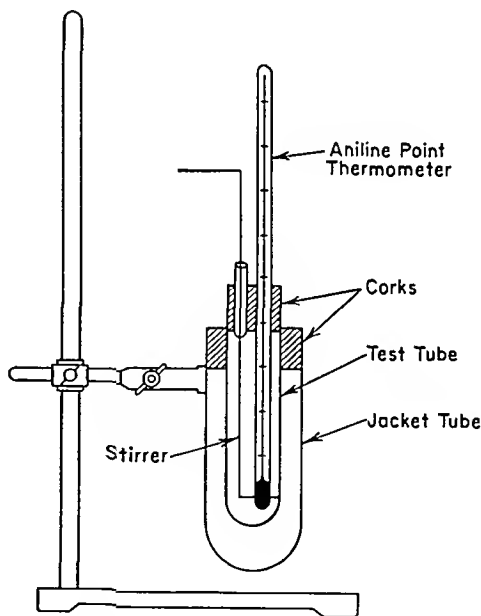


FIG. 40-27. Aniline Point Apparatus.

<sup>22</sup> Approved as ASTM D611-55T.

If the aniline point is below the dew point of the atmosphere provide the aniline point tube with a slow stream of dry inert gas to blanket the aniline-sample mixture.

**ASTM Aniline Point Thermometers**, having ranges of  $-36.5$  to  $+107.5^{\circ}\text{F}$ . ( $-38$  to  $+42^{\circ}\text{C}$ .),  $77$  to  $221^{\circ}\text{F}$ . ( $25$  to  $105^{\circ}\text{C}$ .), and  $194$  to  $338^{\circ}\text{F}$ . ( $90$  to  $170^{\circ}\text{C}$ .) and conforming to the requirements for thermometers  $33^{\circ}\text{F}$ . ( $33^{\circ}\text{C}$ .),  $34^{\circ}\text{F}$ . ( $34^{\circ}\text{C}$ .), and  $35^{\circ}\text{F}$ . ( $35^{\circ}\text{C}$ .) as prescribed in ASTM Standard Specifications E1.

**Pipets**, with capacities of  $10 \pm 0.04$  ml. and  $5 \pm 0.02$  ml. Provide a rubber suction bulb for use with one of the 10-ml. pipets when measuring aniline.

**Balance**.—A laboratory balance sensitive to 0.01 g. suitable for weighing the tube and sample when the sample cannot be pipetted conveniently.

**Apparatus for Method II. Thin-Film Apparatus** made of heat-resistant glass and stainless steel, conforming to the dimensions given in Fig. 40-28. A suggested assembly is shown in Fig. 40-29.

All the remainder of the apparatus for Method II, the Heating and Cooling Bath, the Thermometers, the Pipets, and the Balance, is the same as that used for Method I.

**Reagents. Aniline**.—Dry c.p. aniline over potassium hydroxide pellets, decant, and distill fresh on the day of use, discarding the first and last 10%. Aniline thus prepared shall give an aniline point of  $156.7 \pm 0.4^{\circ}\text{F}$ . ( $69.3 \pm 0.2^{\circ}\text{C}$ .) as determined from the average of two independent tests having a difference of not over  $0.2^{\circ}\text{F}$ . ( $0.1^{\circ}\text{C}$ .) when tested with *n*-heptane according to the Procedure below.

**NOTE 3.—Caution**.—Aniline should not be pipetted directly by mouth because of its extreme toxicity. Aniline is also toxic by absorption through the skin, even in very small quantities, and should be handled with great caution.

**NOTE 4**.—As an alternative to distilling the aniline on the day of use, the aniline may be distilled as described above, collecting the distillate in ampoules, sealing the ampoules under vacuum or dry nitrogen and storing in a cool dark place for future use. In either case, rigid precaution must be taken to avoid contamination from atmospheric moisture (NOTE 2). It is believed that under these conditions the aniline will remain unchanged for a period exceeding 6 months.

**Anhydrous Sodium Sulfate**.

*n*-Heptane, conforming to the requirements listed in Table 40-21.

**Sample**.—Dry the sample by shaking vigorously for 3 to 5 minutes with about 10 per cent by volume of a suitable drying agent such as anhydrous calcium sulfate or anhydrous sodium sulfate. Reduce the viscosity of viscous samples by warming

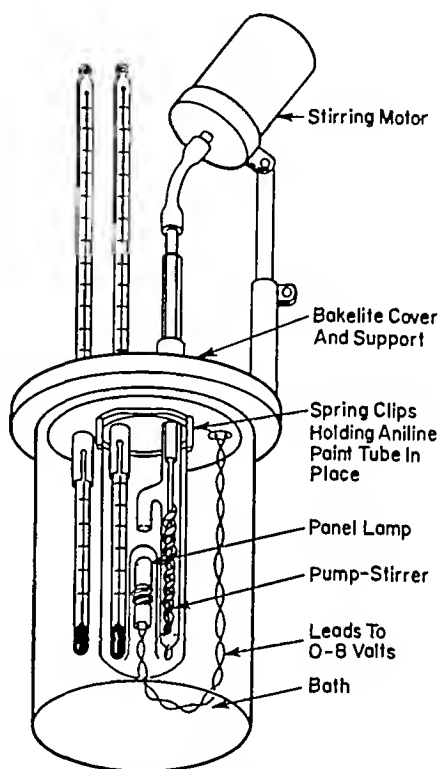


FIG. 40-29. Assembly of Thin-Film Apparatus.

TABLE 40-21 REQUIREMENTS FOR *n*-HEPTANE

ASTM Motor Octane Number <sup>a</sup>	0 0 ± 0 2
Density at 20°C, <sup>b</sup> g per ml	0 68380 ± 0 00015
Refractive Index, <sup>c</sup> $n_D^{20°C}$	1 38770 ± 0 00015
Freezing Point, <sup>d</sup> deg Cent	-90 710 min
Distillation *	
50% Recovered, deg Cent (at 760 mm of Hg)	98 427 ± 0 025
Differential, 80% Recovered minus 20% Recovered, deg Cent	0 020 max

<sup>a</sup> Determined in accordance with ASTM Method D357, Test for Knock Characteristics of Motor Fuels Below 100 Octane Number by the Motor Method

<sup>b</sup> Determined in accordance with ASTM Method D1217, Test for Density and Specific Gravity of Liquids by Bingham Pycnometer

<sup>c</sup> Determined in accordance with ASTM Method D1218, Measurement of Refractive Index and Refractive Dispersion of Hydrocarbon Liquids

<sup>d</sup> Determined in accordance with ASTM Method D1015, Test for Freezing Points of High Purity Hydrocarbons

\* For equipment and method used see *Journal of Research Nat Bureau Standards* 44, No 3 1950 pp 309 and 310 (RP2079)

to a temperature below that which would cause the loss of light ends or the dehydration of the drying agent. Remove any suspended drying agent by centrifugation or filtration. When suspended water is visibly present and when the sample material is known to dissolve less than 0.03 per cent of water by weight, centrifugation for the removal of suspended water is an acceptable procedure.

#### Procedure—General

Two methods to be used as applicable, are covered as follows:

Method 1, described below, is applicable to clear, light colored samples or to samples not darker than No. 6 ASTM color, as determined by ASTM Method D155, Test for Color of Lubricating Oil and Petroleum by Means of ASTM Union Colorimeter.

Method 2, described below, is applicable to light colored samples to moderately dark samples, and to very dark samples.

**Procedure—Method 1.**—Clean and dry the apparatus. Pipet 10 ml of aniline (Caution—See NOTE 3) and 10 ml of the dry sample into the air jacketed tube fitted with stirrer and thermometer. If the material is too viscous for pipeting weigh to the nearest 0.01 g a quantity of the sample corresponding to 10 ml at room temperature. Center the thermometer in the test tube so that the immersion mark is at the liquid level, making sure that the bulb does not touch the side of the tube.

Stir the sample rapidly, using a 2 in stroke, avoiding the inclusion of air bubbles, and, if necessary heating at a rate of approximately 2 to 5°F (1 to 3°C) per minute until complete miscibility is obtained, by applying heat directly to the jacket tube. If the aniline sample mixture is completely miscible at room temperature, substitute a nonaqueous cooling bath for the heating source. Continue stirring and allow the mixture to cool slowly at a rate of 1.0 to 1.8°F (0.5 to 1.0°C)

per minute. Continue cooling to a temperature of 2.0 to 3.5°F. (1 to 2°C.) below the first appearance of turbidity and record as the aniline point the temperature at which the mixture suddenly becomes cloudy throughout (NOTE 5). This will be the minimum equilibrium solution temperature and not the temperature of separation of minor portions of the samples.

NOTE. 5.—The true aniline point is characterized by a turbidity which increases sharply as the temperature is lowered.

Repeat the observation of aniline point temperature by heating and cooling repeatedly until a report as directed under Report can be made.

*Procedure—Method 2.*—Clean and dry the apparatus. Pipet 10 ml. of aniline (*Caution.*—See NOTE 3) and 10 ml. of the sample into the air-jacketed tube fitted with stirrer and thermometer. If the material is too viscous for pipetting, weigh to the nearest 0.01 g. a quantity of sample corresponding to 10 ml., at room temperature. Place the thermometer in the tube so that the contraction chamber is below the liquid level, and so that the mercury bulb does not touch the side of the tube.

Adjust the speed of the pump to produce a continuous stream of the oil-aniline mixture in the form of thin film flowing over the light well. With extremely dark oils, operate the pump slowly and lower it so that the delivery tube nearly touches the top of the light well, thus obtaining a film that is continuous and thin enough to permit observation of the aniline point. Adjust the voltage on the lamp until just enough light is given for the filament to be visible through the film. Raise the temperature of the mixture at a rate of 2.0 to 3.5°F. (1 to 2°C.) per minute until the aniline point has just been passed as denoted by a definite, sudden brightening of the lamp filament, and by the disappearance of the more or less opalescent condition of the film (NOTE 6). Discontinue heating and adjust the lamp voltage so that the filament appears clear and distinct but not uncomfortably bright to the eye. Adjust the temperature of the bath so that the sample-aniline mixture cools at a rate of 1.0 to 1.8°F. (0.5 to 1.0°C.) per minute and note the appearance of the film and light filament. Record as the aniline point the temperature at which a second phase appears as evidenced by the reappearance of the opalescent condition of the film (usually causing a halo to appear around the lamp filament) or by a sudden dimming of the lamp filament, or both.

NOTE 6.—For those making the test for the first time, the following procedure may be helpful: Make preliminary operational adjustments and tests, using a colorless sample-aniline mixture and observing the changes taking place in the body of the liquid and film. Make rough tests with dark oils to become familiar with the appearance of the film and light source as the mixture passes from the clear state above the aniline point to the translucent state below. If the sample is such that there is difficulty in observing the exact point of the phase change, make experiments with the sample, using various intensities of light and paying particular attention to the appearance of the light in the immediate vicinity of the lamp filament.

Repeat the observation of aniline point temperature by heating and cooling repeatedly until a report as directed under Report can be made.

*Procedure for Mixed Aniline Point.*—This procedure is applicable to samples having aniline points below the temperature at which aniline crystallizes from the mixture. Pipet 10 ml. of aniline (*Caution.*—See NOTE 3), 5 ml. of sample, and 5 ml. of *n*-heptane into a clean, dry apparatus. Determine the aniline point of the mixture by Method 1 or 2, as described above.

**Report**—If the range of three successive observations of the aniline point temperature is not greater than  $0.2^{\circ}\text{F}$  ( $0.1^{\circ}\text{C}$ ) for light colored samples or  $0.4^{\circ}\text{F}$  ( $0.2^{\circ}\text{C}$ ) for dark samples report the average temperature of these observations, corrected for thermometer calibration errors, to the nearest  $0.1^{\circ}\text{F}$  ( $0.05^{\circ}\text{C}$ ) as the aniline point

If such a range is not obtained after five observations repeat the test using fresh quantities of aniline and sample in a clean, dry apparatus and if consecutive temperature observations show a progressive change, or if the range of observations is greater than the repeatability given below, report the method as being inapplicable

**Precision**—The following data should be used for judging the acceptability of results (95% probability)

**Repeatability**—Duplicate results that is two average temperatures obtained by the same operator in a series of observations as described in the preceding section, should be considered suspect if they differ by more than the following amounts

	Repeatability
Aniline Point of	
Clear, light colored samples	$0.3^{\circ}\text{F}$ ( $0.16^{\circ}\text{C}$ )
Moderately dark to very dark samples	$0.6^{\circ}\text{F}$ ( $0.3^{\circ}\text{C}$ ) <sup>a</sup>
Mixed Aniline Point of	
Clear, light colored samples	$0.3^{\circ}\text{F}$ ( $0.16^{\circ}\text{C}$ ) <sup>a</sup>
Moderately dark to very dark samples	$0.6^{\circ}\text{F}$ ( $0.3^{\circ}\text{C}$ ) <sup>a</sup>

<sup>a</sup> Not determined from recent cooperative tests, however, the ratios with those given in the 1953 version are believed to apply

**Reproducibility**—When a result is submitted by each of two laboratories, these two results should not be considered suspect unless they differ by more than the following amounts

	Reproducibility
Aniline Point of	
Clear, light-colored samples	$0.9^{\circ}\text{F}$ ( $0.5^{\circ}\text{C}$ )
Moderately dark to very dark samples	$1.8^{\circ}\text{F}$ ( $1.0^{\circ}\text{C}$ ) <sup>a</sup>
Mixed Aniline Point of	
Clear, light-colored samples	$1.3^{\circ}\text{F}$ ( $0.7^{\circ}\text{C}$ ) <sup>a</sup>
Moderately dark to very dark samples	$1.8^{\circ}\text{F}$ ( $1.0^{\circ}\text{C}$ ) <sup>a</sup>

<sup>a</sup> Not determined from recent cooperative tests, however, the ratios with those given in the 1953 version are believed to apply

## NEUTRALIZATION VALUE (ACID AND BASE NUMBERS) OF PETROLEUM PRODUCTS<sup>23</sup>

### POTENTIOMETRIC TITRATION METHOD

This method describes procedures for the determination of acidic or basic constituents in petroleum products and lubricants (NOTE 1). The method resolves these constituents into groups having weak-acid, strong-acid, weak-base, and strong-base ionization properties, provided the dissociation constants of the more strongly acidic or basic compounds are at least 1000 times that of the next weaker groups.

NOTE 1.—In new and used oils, the constituents that may be considered to have acidic characteristics include organic and inorganic acids, esters, phenolic compounds, lactones, resins, salts of heavy metals, salts of ammonia and other weak bases, acid salts of polybasic acids, and addition agents such as inhibitors and detergents. Similarly, constituents that may be considered to have basic properties include organic and inorganic bases, amino compounds, salts of weak acids (soaps), basic salts of polyacidic bases, salts of heavy metals, and addition agents such as inhibitors and detergents.

The method may be used to indicate relative changes that occur in an oil during use under oxidizing conditions regardless of the color or other properties of the resulting oil (NOTE 2). Although the titration is made under definite equilibrium conditions, the method is not intended to measure an absolute acidic or basic property that can be used to predict performance of an oil under service conditions. No general relationship between bearing corrosion and acid or base number is known.

NOTE 2.—A color-indicator titration method is also available in the ASTM Method D974, Tentative Method of Test for Neutralization Value (Acid and Base Numbers) by Color-Indicator Titration. The acid and base numbers obtained by the potentiometric method may or may not be numerically the same as those obtained by Method D974 or equivalent color indicator methods such as given in Federal Test Method Std. No. 791.

**Definitions and Descriptions of Terms.** **Total Acid Number.**—The quantity of base, expressed in milligrams of potassium hydroxide, that is required to neutralize all acidic constituents present in 1 g. of sample.

**Strong Acid Number.**—The quantity of base, expressed in milligrams of potassium hydroxide, that is required to neutralize the strong acid constituents present in 1 g. of sample.

**Total Base Number.**—The quantity of acid, expressed in terms of the equivalent number of milligrams of potassium hydroxide, that is required to neutralize all basic constituents present in 1 g. of sample.

**Strong Base Number.**—The quantity of acid, expressed in terms of the equivalent number of milligrams of potassium hydroxide, that is required to neutralize the strong base constituents present in 1 g. of sample.

**Summary of Method.**—The sample is dissolved in a mixture of toluene and isopropyl alcohol containing a small amount of water and titrated potentiometrically with alcoholic potassium hydroxide or hydrochloric acid solution, using a glass indicating electrode and a calomel reference electrode. The meter readings are plotted against the respective volumes of titrating solution and the end points are taken at the inflections in the resulting curve. When no definite inflections are obtained, end points are taken at meter readings corresponding to those found for standard nonaqueous acidic and basic buffer solutions.

<sup>23</sup> Standardized as ASTM D664-58 and ASA No.: Z11.59-1958.



**Apparatus**—The apparatus <sup>4</sup> should consist of the following

**Meter**—A voltmeter or potentiometer that will operate with an accuracy of plus or minus 0.005 % and a sensitivity of plus or minus 0.002 % over a range of at least plus or minus 0.5 % when the meter is used with the electrodes specified in the following paragraphs below and when the resistance between the electrodes falls within the range of 0.2 to 20 megohms. The meter should be protected from stray electrostatic fields so that no permanent change in the meter readings over the entire operating range is produced by touching with a grounded <sup>5</sup> lead any part of the exposed surface of the glass electrode, the glass electrode lead, the titration stand or the meter. A desirable apparatus may consist of a continuous reading electronic voltmeter with specified range accuracy and sensitivity that is designed to operate on an input of less than  $5 \times 10^{-12}$  amp when an electrode system having 1000 megohms resistance is connected across the meter terminals that is provided with a metal shield connected to the ground <sup>16</sup> and that is provided with a satisfactory terminal to connect the shielded connection wire from the glass electrode to the meter without interference from the presence of external electrostatic fields.

**Glass Electrode**—A pencil type glass electrode (C Fig 40.30) 125 to 180 mm in length and 8 to 14 mm in diameter. The body of the electrode shall be made of a chemically resistant glass tube with a wall thickness of 1 to 3 mm. The end dipping into the solution shall be closed with a hemisphere of Corning 015 glass sealed on to the electrode tube and the radius of this hemisphere shall be about 7 mm. The thickness of the glass in the hemisphere shall be great enough so that the resistance of the hemisphere is 100 to 1000 megohms at 25°C. The electrode should contain a reproducible permanently sealed liquid cell for making electrical connection with the inner surface of the hemisphere. The entire electrical connection from the sealed contact cell to the meter terminal should be surrounded by an electrical shield that will prevent electrostatic interference when the shield is grounded. The shield should be insulated from the electrical connection by insulating material of the highest quality such as rubber and glass so that the resistance between the shield and the entire length of the electrical connection is greater than 50,000 megohms.

**Calomel Electrode**—A pencil type calomel electrode (B Fig 40.30) 125 to 180 mm in length and 8 to 14 mm in diameter. This electrode shall be made of glass and shall be provided with an external removable glass sleeve on the sealed end that is dipped into the titration solution. The glass sleeve shall be 8 to 25 mm in length, shall be slightly tapered and shall be ground to fit the electrode so that the sealed end of the electrode protrudes 2 to 20 mm beyond the sleeve. The ground surface shall be continuous and free of smooth spots. At a point midway between the extremities of the ground surface the electrode tube shall be pierced by a hole or holes 1 mm in diameter. The electrode shall contain the necessary mercury calomel and electrical connection to the mercury all arranged in a permanent manner. The electrode shall be filled almost to capacity with saturated KCl electrolyte and shall be equipped with a stoppered port through which the

<sup>24</sup> The Beckman pH meter (Model M or G) manufactured by the National Technical Laboratories Pasadena, Cal. and the Dual Titmmeter manufactured by the Precision Scientific Co. Chicago 47 Ill. are suitable.

<sup>25</sup> Grounded or connected to the ground means connected through a resistance of not more than 100 ohms to a standard ground potential such as that of a water service pipe.

electrolyte may be replenished. When suspended in the air and with the sleeve in place, the electrode shall not leak electrolyte at a rate greater than one drop in 10 minutes.

**Stirrer.**—A variable-speed mechanical stirrer of any suitable type, equipped with a glass, propeller-type stirring paddle (*D*, Fig. 40-30). A propeller with blades 6 mm. in radius and set at a pitch of 30 to 45° is satisfactory. If electrical stirring apparatus is used, it must be electrically correct and grounded so that connecting or disconnecting the power to the motor will not produce a permanent change in meter reading during the course of the titration.

**Buret.**—A 10-ml. buret (*E*, Fig. 40-30) graduated in 0.05-ml. division, and calibrated with an accuracy of plus or minus 0.02 ml. The buret shall have a glass stopcock and shall have a tip that extends 100 to 130 mm. beyond the stopcock.

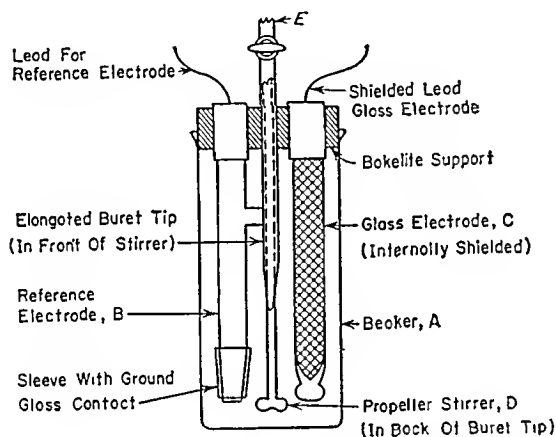


FIG. 40-30. Cell for Potentiometric Titration.

**Titration Beaker.**—A 300-ml. tall-form, lipless beaker (*A*, Fig. 40-30) made of chemically resistant glass. The beaker shall be 116 to 120 mm. in length, and  $62 \pm 3$  mm. inside diameter below the flared portion with sides tapering in at an angle of approximately 1° from the vertical.

**Titration Stand.**—A suitable stand to support the electrodes, stirrer, and buret in the position shown in Fig. 40-30. An arrangement that allows the removal of the beaker without disturbing the electrodes, buret, and stirrer is desirable.<sup>26</sup>

**Purity of Reagents.**—Reagent-grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available.<sup>26a</sup> Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

<sup>26</sup> Such an arrangement is described by L. Lykken and F. B. Rolfson, Potentiometric Titration Stand Assembly, Ind. Eng. Chem., Anal. Ed., 13, 653 (1941).

<sup>26a</sup> Reagent Chemicals, American Chemical Society Specifications, Am. Chem. Soc., Washington, D. C. For suggestions on the testing of reagents not listed by the American Chemical Society, see Reagent Chemicals and Standards, by Joseph Rosin, D. Van Nostrand Co., Inc., Princeton, N. J., and the United States Pharmacopoeia.

Unless otherwise indicated references to water should be understood to mean distilled water

**Reagents Buffer, Nonaqueous Acidic**—Add 10 ml of buffer stock solution A to 100 ml of titration solvent Use within 1 hour

**Buffer, Nonaqueous Basic**—Add 10 ml of buffer stock solution B to 100 ml of titration solvent Use within 1 hour

**Buffer Stock Solution A**—Accurately weigh  $242 \pm 0.1$  g of 2,4,6-trimethyl pyridine ( $\gamma$ -collidine) and transfer to a 1 liter volumetric flask containing 100 ml of isopropyl alcohol Using a 1 liter graduated cylinder add to the flask while continuously stirring its contents  $150/N_1 \pm 5$  ml of 0.2 N alcoholic HCl solution ( $N_1$  being the exact normality of the HCl solution found by standardization) Dilute to the 1000 ml mark with isopropyl alcohol and mix thoroughly

**Buffer Stock Solution B**—Accurately weigh  $278 \pm 0.1$  g of *m*-nitrophenol and transfer to a 1 liter volumetric flask containing 100 ml of isopropyl alcohol Using a 250 ml graduated cylinder add to the flask while continuously stirring its contents  $50/N_2 \pm 1$  ml of 0.2 N alcoholic KOH solution ( $N_2$  being the exact normality of the KOH solution found by standardization) Dilute to the 1000 ml mark with isopropyl alcohol and mix thoroughly

**Hydrochloric Acid Solution, Standard Alcoholic (0.1 N)**—Mix 9 ml of hydrochloric acid (HCl sp gr 1.19) with 1 liter of anhydrous isopropyl alcohol Standardize frequently enough to detect normality changes of 0.0005 by potentiometric titration of approximately 8 ml (accurately measured) of the 0.1 N alcoholic KOH solution diluted with 125 ml of  $\text{CO}_2$  free water

**Hydrochloric Acid Solution, Standard Alcoholic (0.2 N)**—Prepare and standardize as directed in preceding paragraph but use 18 ml of HCl (sp gr 1.19)

**Potassium Chloride Electrolyte**—Prepare a saturated solution potassium chloride (KCl) in water

**Potassium Hydroxide Solution Standard Alcoholic (0.1 N)**—Add 6 g of potassium hydroxide (KOH) to approximately 1 liter of anhydrous isopropyl alcohol Boil gently for 10 minutes to effect solution Allow the solution to stand for two days and then filter the supernatant liquid through a fine sintered glass funnel Store the solution in a chemically resistant bottle Dispense in a manner such that the solution is protected from atmospheric carbon dioxide ( $\text{CO}_2$ ) by means of a guard tube containing soda lime or soda asbestos (Ascarite), and such that it does not come into contact with cork rubber or saponifiable stopcock grease Standardize frequently enough to detect normality changes of 0.0005 by potentiometric titration of weighed quantities of potassium acid phthalate dissolved in  $\text{CO}_2$  free water

**Potassium Hydroxide Solution, Standard Alcoholic (0.2 N)**—Prepare store and standardize as directed in preceding paragraph but use 12 to 13 g of KOH to approximately 1 liter of isopropyl alcohol

**Titration Solvent**—Add 500 ml of toluene and 5 ml of water to 495 ml of anhydrous isopropyl alcohol The titration solvent should be made up in large quantities and its blank value determined daily by titration prior to use

**Preparation of Electrode System Maintenance of Electrodes**—Clean the glass electrode (NOTE 3) at frequent intervals (not less than once every week during continual use) by immersing in cold chromic acid cleaning solution Drain the calomel electrode at least once each week and refill with fresh KCl electrolyte Maintain the electrolyte level in the calomel electrode above that of the liquid in the titration beaker at all times When not in use, immerse the lower halves of the electrodes in water Do not allow them to remain immersed in titration solvent for

any appreciable period of time between titrations. While the electrodes are not extremely fragile, handle them carefully at all times.

**Preparation of Electrodes.**—Before and after using, wipe the glass electrode thoroughly with a clean cloth, or a soft absorbent tissue, and rinse with water. Wipe the calomel reference electrode with a cloth or tissue, carefully remove the ground-glass sleeve, and thoroughly wipe both ground surfaces. Replace the sleeve loosely and allow a few drops of electrolyte to drain through to flush the ground-glass joint (NOTE 3). Wet the ground surfaces thoroughly with electrolyte, set the sleeve firmly in place, and rinse the electrode with water. Prior to each titration, soak the prepared electrodes in water for at least 5 minutes immediately before use, and touch the tips of the electrodes with a dry cloth or tissue to remove the excess water.

**Testing of Electrodes.**—Test the meter-electrode combination (NOTE 3) when first put into use, or when new electrodes are installed, and retest at intervals thereafter by dipping the electrodes into a well-stirred mixture of 100 ml. of the titration solvent and 1.0 to 1.5 ml. of 0.1 *N* alcoholic KOH solution. For the meter-electrode combination to be suitable for use, the potential between the electrodes should change by more than 0.480 v. from the potential between the same electrodes when dipped in the nonaqueous acidic buffer solution (NOTE 4).

NOTE 3.—Cleaning the electrodes thoroughly, keeping the ground-glass joint free of foreign materials, and regular testing of the electrodes are very important in obtaining reproducible potentials, since contamination may introduce uncertain, erratic, and unnoticeable liquid contact potentials.<sup>27</sup> While this is of secondary importance when end points are chosen from inflection points in the titration curve, it may be quite serious when end points are chosen at arbitrarily-fixed cell potentials.

NOTE 4.—Considerably more sensitive electrodes are now available that will show a potential change of at least 0.590 v. under these conditions, and their use is recommended.

**Standardization of Apparatus.** **Determination of Meter Readings for the Non-aqueous Buffer Solutions Corresponding to Acid and Base End Points.**—To insure comparable selection of end points when definite inflection points are not obtained in the titration curve, determine daily, for each electrode pair, the meter readings obtained with the nonaqueous acidic and basic buffer solutions (NOTE 5).

Prepare the electrodes as described above, immerse them in the nonaqueous buffer solution, and stir for 5 minutes, maintaining the temperature of the buffer solution at a temperature within 2°C. of that at which the titrations are to be made. Read the cell voltage. The readings so obtained are taken as the end points in titration curves having no inflection points.

NOTE 5.—The response of different glass electrodes to hydrogen ion activity is not the same. Therefore, it is necessary to establish regularly for each electrode system the meter readings corresponding to the buffer solutions arbitrarily selected to represent acidic or basic end points.

**Preparation of Sample of Used Oil.**—Strict observance of the sampling procedure is necessary, since the sediment itself is acidic or basic or has adsorbed acidic or basic material from the sample. Failure to obtain a representative sample causes serious errors.

<sup>27</sup> For a detailed discussion of the need for care in preparation of the electrodes, see L. Lykken, P. Porter, H. D. Ruliffson, and F. D. Tuemmler, "Potentiometric Determination of Acidity in Highly Colored Oils," Industrial and Engineering Chemistry, Analytical Edition, Vol. 16, pp. 219-234 (1944).

NOTE 6—As used oil may change appreciably in storage samples should be tested as soon as possible after removal from the lubricating system and the dates of sampling and testing should be noted.

Heat the sample (NOTE 7) of used oil to  $60 \pm 5^\circ\text{C}$  in the original container until all of the sediment is homogeneously suspended in the oil. If the original container is a can or if it is glass and more than three fourths full transfer the entire sample to a clear glass bottle having a capacity at least one third greater than the volume of the sample. Transfer all traces of sediment from the original container to the bottle by violent agitation of portions of the sample in the original container.

NOTE 7—When samples are visibly free of sediment the heating procedures described may be omitted.

After complete suspension of all sediment strain the sample or a convenient aliquot through a 100 mesh screen for the removal of large contaminating particles.

**Procedure for Total Acid Number and Strong Acid Number**—Into a 300 ml titration beaker introduce a weighed quantity of sample as prescribed in Table 40.22 and add 125 ml of titration solvent (NOTE 8). Prepare the electrodes as

TABLE 40.22 SIZE OF SAMPLE

Acid Number or Base Number	Size of Sample g	Sensitivity of Weighing g
0.05 to 1.0	$20.0 \pm 2.0$	0.10
1.0 to 5.0	$5.0 \pm 0.5$	0.02
5 to 20	$1.0 \pm 0.1$	0.005
20 to 100	$0.25 \pm 0.02$	0.001
100 to 250	$0.1 \pm 0.01$	0.0005

directed above. Place the beaker on the titration stand and adjust its position so that the electrodes are about half immersed. Start the stirrer and stir throughout the determination at a rate sufficient to produce vigorous agitation without spitting and without stirring air into the solution.

NOTE 8—A titration solvent in which chloroform is used in place of toluene may be required to completely dissolve certain heavy residues or asphaltic materials.

Fill the buret with the 0.1 N alcoholic KOH solution and place the buret in position in the titration assembly taking care that the tip is immersed about 1 in in the liquid in the beaker. Record the initial buret and meter (cell potential) readings. Add suitable small portions of 0.1 N alcoholic KOH solution and after waiting until a constant potential has been established (see NOTE 9) record the buret and meter readings. At the start of the titration and in any subsequent regions (inflections) where 0.1 ml of 0.1 N KOH solution consistently produces a total change of more than 0.03 v (corresponding to 0.5 pH scale units) in the cell potential add 0.05 ml portions. In the intermediate regions (plateaus) where 0.1 ml changes the cell potential less than 0.03 v add larger portions sufficient to

produce a total potential change approximately equal to, but not greater than, 0.03 v. Titrate in this manner until the potential changes less than 0.005 v. (corresponding to 0.1 pH scale units) per 0.1 ml. and the cell potential indicates that the solution is more basic than the nonaqueous basic buffer. Remove the titrated solution, rinse the electrodes with isopropyl alcohol, and immerse the electrodes in distilled water.

NOTE 9.—Consider the cell potential constant when it changes less than 0.005 v. (corresponding to 0.1 pH scale units) per minute. This may require approximately 1 to 2 minutes per 0.1-v. change in potential (corresponding to 1.7 pH scale units) when adding 0.05-ml. increments; 1-ml. increments may require 3 to 5 minutes.

Blank.—For each set of samples, make a blank titration of 125 ml. of titration solvent, adding 0.1 *N* alcoholic KOH solution in 0.05-ml. increments and recording meter and buret readings when the former becomes constant after each increment.

*Procedure for Base Number and Strong Base Number.*—Proceed as directed under Preparation of Sample of Used Oil, above, but titrate with 0.1 *N* alcoholic HCl solution; add the HCl at the same rate as specified for the KOH solution.

Blank.—For each set of samples, make a blank titration of 125 ml. of titration solvent, adding 0.1 *N* alcoholic HCl solution in 0.05-ml. increments in a manner comparable to that specified under Blank, above.

Calculations.—Plot the volumes of the acid or base titrating solution, or both (NOTE 10), added against the corresponding meter readings (see Fig. 40-31). Mark as an end point any inflection point (NOTE 11) on the curve that occurs near the cell voltages representing the nonaqueous acidic and basic buffers. If no inflection appears, mark the end points at those meter readings corresponding to the two nonaqueous buffers.

NOTE 10.—An oil may have both a weak-acid number and a weak-base number if the initial meter reading falls between the readings of the acidic and basic nonaqueous buffers. If the initial meter reading indicates that the solution is more basic than the basic buffer or more acidic than the acid buffer, the oil may contain mixtures of strong and weak bases, or strong and weak acids, respectively.

NOTE 11.—An inflection point is generally recognizable by inspection whenever several successive 0.05-ml. increments each produce a cell potential change greater than 0.015 v. (corresponding to 0.25 pH scale units) and at least 30% greater than those produced by previous or subsequent increments of the same size. Generally, definite inflection points may be discerned only in regions where increments of the same size are used.

Calculate the total acid number and strong acid number as follows:

$$\text{Total acid number, mg. KOH per g.} = \frac{(A - B) \times N \times 56.1}{W}$$

$$\text{Strong acid number, mg. KOH per g.} = \frac{(CN - Dn) \times 56.1}{W}$$

where *A* = milliliters of alcoholic KOH solution used to titrate to an end point that occurs at the meter reading corresponding to the basic nonaqueous buffer,

*B* = volume corresponding to *A* for the blank titration,

*N* = normality of the alcoholic KOH solution,

*n* = normality of the alcoholic HCl solution,

*W* = grams of sample,

*C* = milliliters of alcoholic KOH solution used to titrate to an end point that occurs at a meter reading corresponding to the acidic nonaqueous buffer, and

*D* = milliliters of alcoholic HCl solution used to titrate the solvent blank to the end point corresponding to *C*.

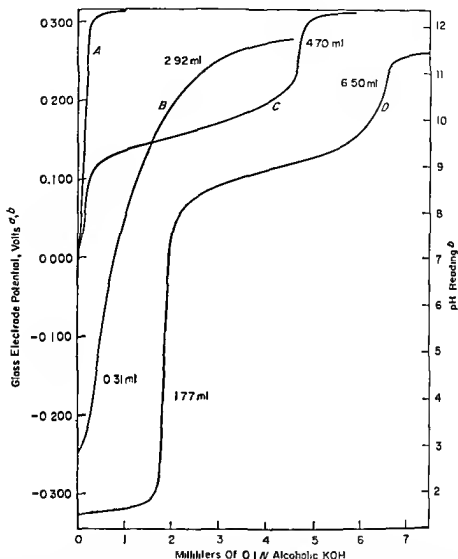


FIG. 10.31 Illustrative Titration Curves. *A*, Blank on 125 ml of titration solvent. *B*, 10.00 g of used crankcase oil plus 125 ml of titration solvent. Since no sharp inflections are apparent the end points are chosen at the meter readings which were obtained with the two nonaqueous buffers. *C*, 10.00 g of oil containing a weak acid plus 125 ml of titration solvent. The end point is chosen at the most vertical portion of the inflection. *D*, 10.00 g of oil containing weak and strong acids plus 125 ml of titration solvent. The end points are chosen at the most vertical portions of the two inflections.

<sup>a</sup> On some meters, the voltage sign is reversed.

<sup>b</sup> In some instruments the relation between glass electrode potential and pH reading is only approximately as shown.

Calculate the total base number and strong base number as follows:

$$\text{Total base number, mg. KOH per g.} = \frac{(E - F) \times N \times 56.1}{W}$$

$$\text{Strong base number, mg. KOH per g.} = \frac{(GN - Hn) \times 56.1}{W}$$

where  $E$  = milliliters of alcoholic HCl solution used to titrate to an end point which occurs at a meter reading corresponding to the acidic nonaqueous buffer,

$F$  = volume corresponding to  $E$  for the blank titration,

$N$  = normality of the HCl solution.

$n$  = normality of the alcoholic KOH solution,

$W$  = grams of sample,

$G$  = milliliters of alcoholic HCl solution used to titrate to an end point that occurs at a meter reading corresponding to the basic nonaqueous buffer, and

$H$  = milliliters of alcoholic KOH solution used to titrate the solvent blank to the end point corresponding to  $G$ .

**Precision. Good Inflection in Titration Curve.**—When good inflections are obtained in the titration curves, results should not differ from the mean by more than the following amounts:

Acid or Base Number	Repeatability	Reproducibility
0.05 to 1.0	0.02	0.04
1.0 to 5.0	0.1	0.2
5 to 20	0.5	1
20 to 100	2	4
100 to 250	5	10

**Poor Inflection in Titration Curve**—When poor inflections are obtained in the titration curves, the values for repeatability and reproducibility will be larger than those given above.

## CONRADSON CARBON RESIDUE OF PETROLEUM PRODUCTS<sup>28</sup>

This method describes a procedure for the determination of the amount of carbon residue (NOTE 1) left after evaporation and pyrolysis of an oil, and is intended to provide some indication of relative coke-forming propensities. The method is generally applicable to relatively nonvolatile petroleum products which partially decompose on distillation at atmospheric pressure. Petroleum products containing ash-forming constituents as determined by ASTM Method D482, Test for Ash from

<sup>28</sup> Standardized as ASTM D189-61 and ASA No.: Z11.25-1961.



Petroleum Oils, will have an erroneously high carbon residue depending upon the amount of ash formed

**NOTE 1**—The term **carbon residue** is used throughout this method to designate the carbonaceous residue formed after evaporation and pyrolysis of a petroleum product. The residue is not entirely composed of carbon, but is a coke which can be further changed by pyrolysis. The term **carbon residue** is continued in this method only in deference to its wide common usage.

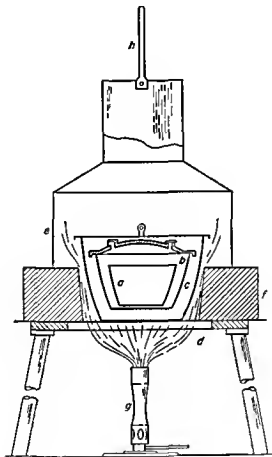


FIG 40 32 Apparatus for Determining Carbon Residue

**NOTE 2**—Values obtained by this method are not numerically the same as those obtained by ASTM Method D524 Test for Ramsbottom Carbon Residue of Petroleum Products nor have satisfactory correlations been found between the results by the two methods for all materials which may be tested because the carbon residue test is applied to a wide variety of petroleum products

**Apparatus.**—The apparatus (see Fig 40 32) should consist of the following

**Porcelain Crucible.**—Porcelain crucible, *a*, wide form, glazed throughout or a silica crucible, 29 to 31 ml capacity, 46 to 49 mm (1 81 to 1 93 in) in rim diameter

**Iron Crucible.**—Skidmore iron crucible, *b*, flanged and ringed, 65 to 82 ml capacity, 53 to 57 mm (2 07 to 2 20 in) inside and 60 to 67 mm (2 36 to 2 64 in) outside diameter of flange, 37 to 39 mm (1 46 to 1 54 in) in height supplied with

a cover without delivery tubes and having the vertical opening closed. The horizontal opening of about 6.5 mm. (0.26 in.) shall be kept clean. The outside diameter of the flat bottom shall be 30 to 32 mm. (1.18 to 1.26 in.).

**Iron Crucible.**—Spun sheet-iron crucible, *c*, with cover; 78 to 82 mm. (3.07 to 3.23 in.) in outside diameter at the top, 58 to 60 mm. (approximately 2.3 in.) in height, and approximately 0.8 mm. (0.03 in.) in thickness. Place at the bottom of this crucible, and level before each test, a layer of about 25 ml. of dry sand, or enough to bring the Skidmore crucible, with cover on, nearly to the top of the sheet-iron crucible.

**Wire Support.**—Triangle of bare Nichrome wire, *d*, of approximately No. 13 B & S gage having an opening small enough to support the bottom of the sheet-iron crucible at the same level as the bottom of the asbestos block or hollow sheet-metal box (see Insulator, below).

**Hood.**—Circular sheet-iron hood, *e*, from 120 to 130 mm. ( $4\frac{3}{4}$  to  $5\frac{1}{4}$  in.) in diameter the height of the lower perpendicular side to be from 50 to 53 mm. (2 to  $2\frac{1}{8}$  in.); provided at the top with a chimney 50 to 60 mm. (2 to  $2\frac{1}{2}$  in.) in height and 50 to 56 mm. (2 to  $2\frac{1}{4}$  in.) in inside diameter, which is attached to the lower part having the perpendicular sides by a cone-shaped member, bringing the total height of the complete hood to 125 to 130 mm. ( $4\frac{7}{8}$  to  $5\frac{1}{8}$  in.). The hood may be made from a single piece of metal, provided it conforms to the foregoing dimensions. As a guide for the height of the flame above the chimney, a bridge, *h*, made of approximately 3-mm. ( $\frac{3}{8}$ -in.) iron or Nichrome wire, and having a height of 50 mm. (2 in.) above the top of the chimney, shall be attached.

**Insulator.**—Asbestos block, refractory ring, or hollow sheet-metal box, 150 to 175 mm. (6 to 7 in.) in diameter if round, or on a side if square, 32 to 38 mm. ( $1\frac{1}{4}$  to  $1\frac{1}{2}$  in.) in thickness, provided with a metal-lined, inverted cone-shaped opening through the center; 83 mm. ( $3\frac{3}{4}$  in.) in diameter at the bottom, and 89 mm. ( $3\frac{1}{2}$  in.) in diameter at the top. In the case of the refractory ring no metal lining is necessary, providing the ring is of hard, heat-resistant material.

**Burner.**—Burner, *g*, Meker type, 24 mm. (1 in.) in diameter by 155 mm. (6 in.) in height, suitable for either manufactured or natural gas.

**Procedure.**—Weigh to the nearest 5 mg. a 10-g. sample of the oil to be tested, free of moisture and other suspended matter, into a tared porcelain or silica crucible containing two glass beads about 0.1 in. in diameter. Place this crucible in the center of the Skidmore crucible. Level the sand in the large sheet-iron crucible and set the Skidmore crucible on it in the exact center of the iron crucible. Apply covers to both the Skidmore and the iron crucible, the one on the latter fitting loosely to allow free exit to the vapors as formed.

On a suitable stand or ring, place the bare Nichrome wire triangle and on it the insulator. Next center the sheet-iron crucible in the insulator with its bottom resting on top of the triangle, and cover the whole with the sheet-iron hood in order to distribute the heat uniformly during the process (see Fig. 40-32).

Apply heat with a high, strong flame from the Meker-type gas burner, so that the preignition period will be  $10 \pm 1.5$  minutes (a shorter time may start the distillation so rapidly as to cause foaming or too high a flame). When smoke appears above the chimney, immediately move or tilt the burner so that the gas flame plays on the sides of the crucible for the purpose of igniting the vapors. Then remove the heat temporarily, and before replacing adjust by screwing down the pinch-cock

Add to the Erlenmeyer flask, while still warm, the residue left in the distillation flask, and shake well.

The contents of the Erlenmeyer flask then represent a 10% residuum from the original product. While warm enough to flow freely, pour approximately 10 g. of the residuum into the weighed crucible to be used in the carbon residue test.

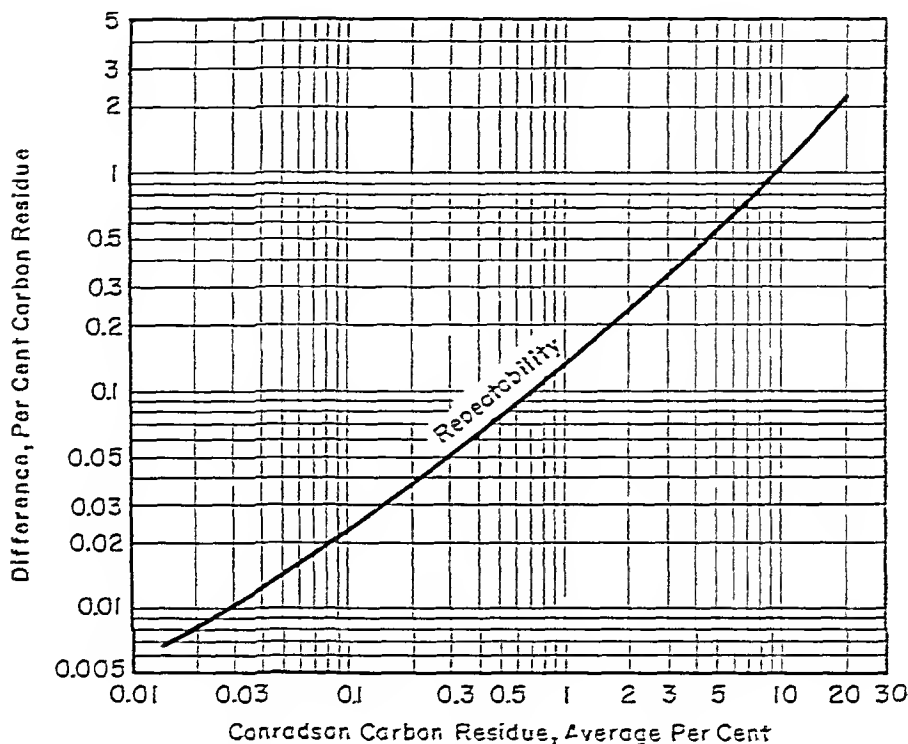


FIG. 40-33. Repeatability versus Average Per Cent Residue, Conradson Carbon Residue.

After cooling, determine the weight of the sample accurately, and carry out the carbon residue test in accordance with the procedure described under Procedure. Report the percentage of carbon residue in the residuum as "carbon residue on 10% residuum."

**NOTE.**—It is important that a clean distillation flask be used for each test.

**Precision.**—The data shown in Figs. 40-33 and 40-34 should be used for judging the acceptability of the results when testing homogeneous samples.

**Repeatability.**—Duplicate results by the same operator should be considered suspect if they differ by more than the amounts shown for repeatability.

**Reproducibility.**—The results of two laboratories should not be considered suspect unless they differ by more than the amounts shown for reproducibility.

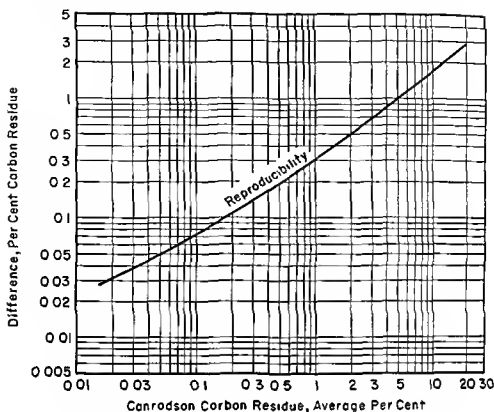


FIG. 40.34 Reproducibility versus Average Per Cent Residue Conradson Carbon Residue

### ASH FROM PETROLEUM OILS <sup>a</sup>

This method describes a procedure for determining the ash from distillate and residual fuel oils, crude oils, lubricating oils, waxes, and other petroleum products in which any ash-forming materials present are normally considered to be undesirable impurities or contaminants (NOTE 1). The method is limited to petroleum products which are free from added ash-forming additives, including certain phosphorus compounds (NOTE 2).

**NOTE 1**—In certain types of samples, all of the ash-forming metals may not be retained quantitatively in the ash. This is particularly true of distillate oils which require a special ash procedure in order to retain metals quantitatively.

**NOTE 2**—This method is not intended for the analysis of new additive-containing lubricating oils. For such samples, use ASTM Method D874, Test for Sulfated Ash from Lubricating Oils and Additives; neither is it intended for the analysis of lubricating oils containing lead nor for used engine crankcase oils. For such samples, use ASTM Method D910, Test for Sulfated Residue, Lead, Iron, and Copper in Lubricating Oils.

**Summary of Method**—The sample contained in a suitable dish is ignited and allowed to burn until only ash and carbon remain. The carbonaceous residue is reduced to an ash by heating in a muffle furnace at 775°C, cooled in a desiccator, and weighed.

<sup>a</sup> Approved as ASTM D482-59T and ASA No. Z11.54-1960.

**Apparatus.** Evaporating Dish, made of platinum or porcelain, of 90- to 120-ml. capacity.

Electric Muffle Furnace capable of maintaining a temperature of  $775 \pm 25^{\circ}\text{C}$ .

**Procedure.**—Heat the evaporating dish at  $700$  to  $800^{\circ}\text{C}$ . for 10 minutes or more. Cool to room temperature in a desiccator, and weigh to the nearest 0.1 mg.

Place an approximately 50-g. sample in the dish and weigh to the nearest 0.1 g. Heat the dish and sample until the contents can be ignited with a flame. Maintain at such a temperature that the sample continues to burn at a uniform and moderate rate, leaving only ash and carbon when the burning ceases.

**NOTE 3.**—If the sample contains sufficient moisture to cause foaming and loss of material, discard the sample, and to an additional sample add 1 to 2 ml. of 99 per cent isopropyl alcohol before heating. If this is not satisfactory, add 10 ml. of an equivolume mixture of benzene and isopropyl alcohol and mix thoroughly. Place several strips of ashless filter paper in the mixture and heat; when the paper begins to burn, the greater part of the water will have been removed.

Heat the residue in the muffle furnace at  $775 \pm 25^{\circ}\text{C}$ . until all carbonaceous material has disappeared. Cool the dish to room temperature in a desiccator, and weigh to the nearest 0.1 mg.

Reheat the dish at  $775^{\circ}\text{C}$ . for 10 to 20 minutes, cool in a desiccator, and reweigh. Repeat the heating and weighing until consecutive weighings differ by not more than 0.5 mg.

**Calculation.**—Calculate the ash from the sample as follows:

$$\text{Ash, per cent} = \frac{w}{W} \times 100$$

where  $w$  = weight of ash, in grams, and

$W$  = weight of sample, in grams.

**Precision.**—The following data should be used for judging the acceptability of results (95% probability):

**Repeatability.**—Duplicate results by the same operator should not be considered suspect unless they differ by more than the following amount:

Ash, Per Cent	Repeatability
0.0 to 0.15.....	0.003

**Reproducibility.**—The results submitted by each of two laboratories should not be considered suspect unless the two results differ by more than the following amount:

Ash, Per Cent	Reproducibility
0.0 to 0.15.....	0.005

## COPPER STRIP CORROSION BY PETROLEUM PRODUCTS <sup>30</sup>

This method describes procedures for the detection of the corrosiveness to copper of aviation gasoline, aviation turbine fuel, automotive gasoline, farm tractor fuel,

<sup>30</sup> Standardized as ASTM D130-56 and ASA No.: Z11.21-1956.

ingots or bars conforming to ASTM Specifications B5, for Electrolytic Copper Wire Bars, Cakes, Slabs, Billets, Ingots, and Ingot Bars. The strips may be used repeatedly but should be discarded when they show pitting or deep scratches that cannot be removed or when the surfaces become deformed.

**Polishing Materials.** silicon-carbide or alumina grit paper of varying degrees of fineness including 240-grit silicon-carbide paper or cloth; also a supply of 150-mesh silicon-carbide grain and pharmaceutical grade absorbent cotton.

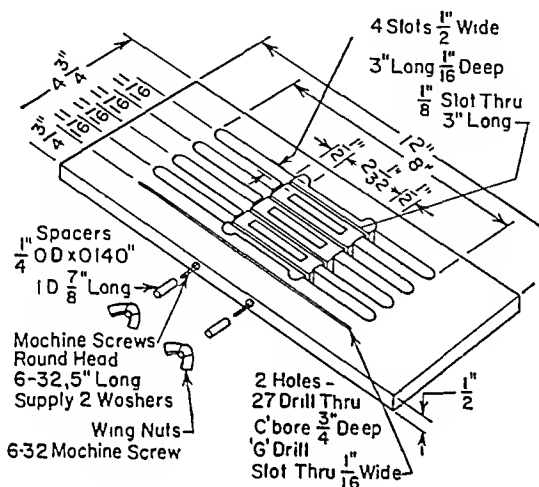


FIG. 40-36. Copper Strip Holder.

**Corrosion Standards.** Copper Corrosion Standard Plaques are available.<sup>31</sup> These consist of reproductions of typical strips representing increasing degrees of tarnish and corrosion as listed under Description in Table 40-23.

NOTE.—These reproductions have been lithographically printed on aluminum sheets and are encased in plastic for protection. Two printings have been made, one dated November 1954, and the second December 1958. Both are identical in significant features and when new, both printings may be considered official standards.

**Preparation of Strips.** Surface Preparation.—Remove all surface blemishes from all six sides of the strip with silicon carbide or alumina grit paper of such degrees of fineness as are needed to accomplish the desired results efficiently (NOTE below). Finish with 240-grit silicon-carbide paper, removing all marks that may have been made by other grades of paper used previously. Immerse the strip in knock test isooctane, from which it may be withdrawn immediately for final polishing or in which it may be stored for future use.

NOTE.—As a practical manual procedure, for surface preparation, place a sheet of the paper on a flat surface, moisten it with kerosene or isooctane, and rub the strip against the paper with a rotary motion, protecting the strip from contact with the fingers with an ashless filter paper. Alternatively, the strip may be prepared by use of motor-driven machines using appropriate grades of dry paper or cloth.

<sup>31</sup> The ASTM Copper Strip Corrosion Standards approved by Committee D-2 are available on order from ASTM Headquarters, 1916 Race St., Philadelphia 3, Pa.

**Final Polishing**—Remove a strip from the isooctane. Holding it in the fingers protected with ashless filter paper, polish first the ends and then the sides with the 150 mesh silicon carbide grains picked up from a clean glass plate with a pad of absorbent cotton moistened with a drop of isooctane. Wipe vigorously with fresh

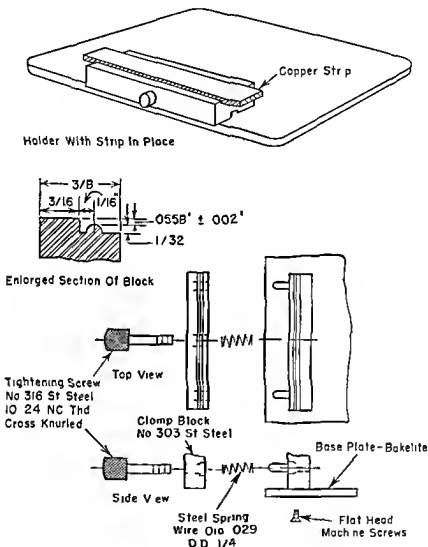


FIG. 4031. Optional Copper Strip Holder

pads of absorbent cotton and subsequently handle only with stainless steel forceps do not touch with the fingers. Clamp in a vise and polish the main surfaces with silicon carbide grains on absorbent cotton. Rub in the direction of the long axis of the strip carrying the stroke beyond the end of the strip before reversing the direction (see NOTE below). Clean all metal dust from the strip by rubbing vigorously with clean pads of absorbent cotton until a fresh pad remains unsoiled. When the strip is clean immediately immerse it in the prepared sample.

**NOTE.**—It is important to polish the whole surface of the strip uniformly to obtain a uniformly stained strip. If the edges show wear (surface elliptical) they will likely show more corrosion than the center. The use of a vise will facilitate uniform polishing.

**Sample.**—It is particularly important that gasoline and fuel samples for this test be collected in clean dark bottles or cleaned tinned cans; to clean new tinned cans, rinse free of rosin or soldering flux with the sample to be tested. Care should be taken during sampling to protect the samples from exposure to direct or even diffused daylight (see **NOTE** below). Make the test as soon as possible after sampling.

**NOTE.**—Short wavelengths of light (violet and ultraviolet) have a marked effect on reducing, or removing entirely, the coloration tendency of the corrosive sulfur present in the sample on copper.

If suspended water (haze) is observed in the sample (see **NOTE** below), dry by filtering a sufficient volume of sample through a medium rapid qualitative filter (for example, Whatman No. 4), into the prescribed clean, dry test tube. Carry out this operation in a darkened room or under a light-protected shield.

**NOTE.**—Contact of the copper strip with water before, during, or after the completion of the test run, will cause staining, making it difficult to evaluate the strips.

**Procedure.** Tests at 122°F. (50°C.) and 212°F. (100°C.) on Less Volatile Materials.—Place 30 ml. of sample, completely clear and free of any suspended or entrained water (**NOTE** above), into a chemically clean, dry 25- by 150-ml. test tube and, within 1 minute after completing the final polishing, slide the copper strip into the sample tube. Stopper with a vented cork and place in a bath maintained at the required temperature within  $\pm 2^\circ\text{F}$ . ( $1^\circ\text{C}$ ). After 3 hours  $\pm 5$  minutes in the bath, examine the strip as described in Examination of Strip, p. 2004.

Tests at 212°F. (100°C.) for Volatile Materials.—Place 30 ml. of sample, completely clear and free of any suspended or entrained water (**NOTE** above) into a chemically clean, dry 25- by 150-mm. test tube, and within 1 minute after completing the final polishing, slide the copper strip into the sample tube. Carefully slide the test tube into the sample bomb (Fig. 40-35) and screw the lid on tight. Completely immerse the bomb in a boiling water bath ( $212 \pm 2^\circ\text{F}$ . or  $100 \pm 1^\circ\text{C}$ ). After 2 hours  $\pm 5$  minutes in the bath, withdraw the bomb, immerse for a few minutes in tap water. Open, withdraw the test tube and examine the strip as described in the following paragraph.

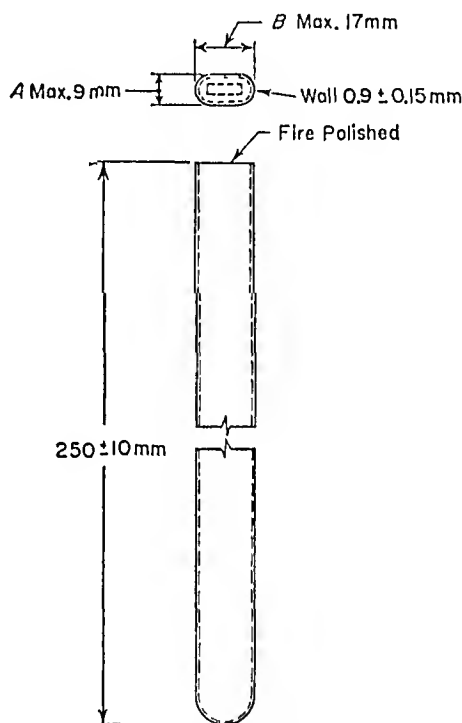


FIG. 40-38. Flat Glass Test Tube. Minimum lengths of *A* and *B* to Be Such That a Copper Strip of  $\frac{1}{8}$  in. by  $\frac{1}{2}$  in. Section Will Enter.



When a strip is in the obvious transition state between that indicated by any two adjacent Corrosion Standard Strips, judge the sample by the more tarnished Standard Strip.

A claret red strip in Classification 2 can be mistaken for a magenta overcast on brassy strip in Classification 3 if the brassy underlay of the latter is completely masked by a magenta overtone. To distinguish, immerse the strip in knock test iso-octane; the former will appear as a dark orange strip while the latter will not change.

To distinguish multicolored strips in Classifications 2 and 3, place a test strip in a 20- by 150-mm. test tube and bring to a temperature of 600 to 700°F. (315 to 355°C.) in 4 to 6 minutes with the tube lying on a hot plate. Adjust to temperature by observing an ASTM high distillation thermometer in a second test tube. If the strip belongs in Classification 2, it will assume the color of a silvery and then a gold strip. If in Classification 3 it will take on the appearance of a transparent black, etc., as described in Classification 4.

Repeat the test if blemishes due to finger prints are observed, or due to spots from any particles or water droplets that may have touched the test strip during the digestion period.

Repeat the test also if the sharp edges along the flat faces of the strip appear to be in a classification higher than the greater portion of the strip; in this case it is likely that the edges were burnished during polishing.

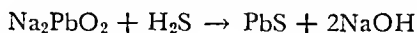
**Report.**—Report the corrosiveness in accordance with one of the four numbered classifications listed in Table 40-23.

## DOCTOR TEST FOR PETROLEUM DISTILLATES

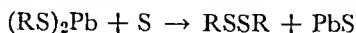
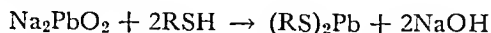
### U.O.P. METHOD 41-59<sup>32</sup>

This method demonstrates the presence of hydrogen sulfide and mercaptans in gasoline and similar distillates.

**Outline of Method.**—The sample is shaken with a sodium plumbite solution in a test tube. If hydrogen sulfide is present the following reaction occurs:



The lead sulfide is black and readily visible. If this reaction does not appear, sulfur is added to the test tube. If mercaptans are present, on shaking the mercaptans undergo a series of reactions coloring the hydrocarbon layer first orange, then red, and brown, and finally a black precipitate of lead sulfide appears. The overall reaction may be written:



**Apparatus.**—Stopper, rubber.

**Test Tube,** 25-ml.

**Reagents.** **Doctor Solution.**—Dissolve 125 g. of sodium hydroxide in 1 liter of distilled water. Add 60 g. of litharge and shake vigorously for 15 minutes. Let

<sup>32</sup> U.O.P. Laboratory Test Methods for Petroleum and Its Products, 4th Ed., Universal Oil Products Co., Des Plaines, Illinois, 45-6 (1959). By permission of the copyright owner.

## 2006 PETROLEUM AND PETROLEUM PRODUCTS

stand overnight Decant or siphon off the clear liquid If the liquid does not settle clear filter it through an asbestos mat Keep the solution in a tightly stoppered bottle Re filter if it becomes cloudy

### Sulfur, Flowers of

**Procedure**—Add 5 ml of doctor solution and 10 ml of sample to the test tube and shake vigorously for 15 seconds Observe any appearance of black lead sulfide If no color appears add a very small pinch of flowers of sulfur to the sample and shake 15 seconds Allow to settle Observe the appearance of the interface and the color of each layer

**Report**—If the sample becomes discolored or if the sulfur film on the interface is noticeably masked report the test positive or the sample sour If the sample remains unchanged in color and the sulfur film is bright yellow or only slightly discolored with grey or flecked with black report the test negative and the sample sweet If an indication of the degree of sourness is desired report the sample according to the degree of discoloration as very sour sour slightly sour or sweet

**Precaution**—Use only sufficient sulfur to form a thin film floating on the interface between the sample and the doctor solution

**Precision**—The following figures are quoted from the reference <sup>33</sup>

Mercaptan	Wt % Sulfur Detected
Ethyl	0.0006
n Propyl	0.0002
n Butyl	0.00002
Phenyl	0.0006

## MERCAPTAN SULFUR IN JET FUELS<sup>33a</sup> (COLOR-INDICATOR METHOD)

This method describes the procedure for the determination of mercaptan sulfur in jet fuels containing from 0.0003 to 0.01% by weight of mercaptan sulfur

**NOTE** An instrumental method gives equivalent results within the precision limits of the method ASTM D1323 Amperometric Potentiometric Method Mercaptan Sulfur in Aviation Turbine Fuels

**Summary of Method**—Excess silver nitrate is added to the sample to form silver mercaptides with the mercaptan sulfur compounds present The excess silver nitrate is determined by titration with ammonium thiocyanate using ferric alum indicator

**Purity of Reagents** Reagent grade chemicals shall be used in all tests Unless otherwise indicated it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society where such specifications are available <sup>34</sup> Other grades may be used provided it

<sup>33</sup> Henderson L M Agruss M S and Ayers G W Jr Ind Eng Chem Anal Ed 12, 1 (1940)

<sup>33a</sup> Standardized as ASTM D1219 61

<sup>34</sup> Reagent Chemicals American Chemical Society Specifications Am Chem Soc Washington D C For suggestions on the testing of reagents not listed by the American Chemical Society see Reagent Chemicals and Standards by Joseph Rosin D Van Nostrand Co Inc Princeton N J and the United States Pharmacopoeia

is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

Unless otherwise indicated, references to water shall be understood to mean distilled water or water of equivalent purity.

**Reagents.** Acid Cadmium Sulfate Solution (150 g. per liter).—Dissolve 150 g. of cadmium sulfate ( $3\text{CdSO}_4 \cdot 8\text{H}_2\text{O}$ ) in water, add 10 ml of  $\text{H}_2\text{SO}_4$  (1:5), and dilute to 1 liter with water.

Alcohol.—95% methanol, 95% ethanol denatured with methanol, or isopropanol.

Ammonium Thiocyanate Standard, Solution (0.025 N).—Dissolve 1.90 g. of ammonium thiocyanate ( $\text{NH}_4\text{CNS}$ ) in water, and dilute to 1 liter. Standardize by titrating with the standard  $\text{AgNO}_3$  solution as described in Procedure, under Analysis of Sample, omitting the sample. Calculate the normality of the  $\text{NH}_4\text{CNS}$  solution as follows:

$$\text{Normality of } \text{NH}_4\text{CNS solution} = \frac{A \times N}{B}$$

where  $A$  = milliliters of  $\text{AgNO}_3$  solution required for titration of the  $\text{NH}_4\text{CNS}$  solution,

$N$  = normality of the  $\text{AgNO}_3$  solution, and

$B$  = milliliters of  $\text{NH}_4\text{CNS}$  solution used.

Ferric Alum Indicator Solution.—Dissolve 40 g. of ferric ammonium sulfate ( $\text{FeNH}_4(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ ) in a mixture of 20 ml. of  $\text{HNO}_3$  (3:5) and 80 ml. of water. Heat to boiling and dilute with 3 volumes of water.

Nitric Acid (3:5).—Mix 3 volumes of concentrated nitric acid ( $\text{HNO}_3$ , sp. gr. 1.42) with 5 volumes of water.

Potassium Chloride, Standard Solution (0.025 N).—Dissolve  $1.8640 \pm 0.0010$  g. of dry (1 hour in oven at  $110^\circ\text{C}$ .) potassium chloride ( $\text{KCl}$ ) in water, and dilute to 1 liter in a volumetric flask.

Silver Nitrate Standard Solution (0.025 N).—Dissolve 4.25 g. of silver nitrate ( $\text{AgNO}_3$ ) in water and dilute to 1 liter. To standardize this solution, pipet  $25 \pm 0.05$  ml. of the 0.025 N  $\text{KCl}$  solution into a 400-ml. beaker. Add 2 to 3 drops of saturated sodium chromate ( $\text{Na}_2\text{CrO}_4$ ) solution. Titrate with  $\text{AgNO}_3$  solution until the precipitate shows the first tint of pink. This color may best be observed through the bottom of the beaker. Calculate the normality of the  $\text{AgNO}_3$  solution as follows:

$$\text{Normality of } \text{AgNO}_3 \text{ solution} = \frac{N \times 25}{A}$$

where  $N$  = normality of the  $\text{KCl}$  solution, and

$A$  = milliliters of  $\text{AgNO}_3$  solution required for titration of the  $\text{KCl}$  solution.

Sulfuric Acid (1:5).—Carefully mix 1 volume of concentrated sulfuric acid ( $\text{H}_2\text{SO}_4$ , sp. gr. 1.84) with 5 volumes of water.

**Procedure.** Determination of Gravity.—Determine the API gravity of the sample and convert to specific gravity; or measure the specific gravity directly, at the temperature at which the test sample is taken, if the sample is to be measured volumetrically (see ASTM Method D287, Test for API Gravity of Petroleum and Its Products (Hydrometer Method), p. 1926.

Test for and Removal of Hydrogen Sulfide.—Test the sample qualitatively for hydrogen sulfide ( $\text{H}_2\text{S}$ ) by shaking 5 ml. of sample with 5 ml. of the  $\text{CdSO}_4$  solution in a test tube. If no precipitate appears, proceed with the analysis of the sample as described in the next paragraph. If a yellow precipitate appears, indi-

cating the presence of  $H_2S$  remove the  $H_2S$  in the following manner Shake in a separatory funnel a volume of sample three to four times that required for analysis with a volume of the  $CdSO_4$  solution half that of the sample Draw off and discard the aqueous phase containing the yellow precipitate Repeat the extraction with another portion of the  $CdSO_4$  solution Again draw off the aqueous phase and wash the sample with three 25 to 30 ml portions of water withdrawing the water after each washing Filter the hydrocarbon through rapid filter paper Test a small portion of the washed sample in a test tube with a few milliliters of the  $CdSO_4$  solution If no further precipitate is formed proceed as in the following paragraph If a precipitate appears repeat the extraction with the  $CdSO_4$  solution and water wash as above until all of the  $H_2S$  has been removed

**Analysis of Sample**—Measure with a pipet or weigh 10 to 100 ml (NOTE) of the original or filtered sample into a 250 ml glass stoppered Erlenmeyer flask Record the volume or weight of sample Dilute the sample with 15 ml of alcohol Add accurately from a buret 15 ml of the  $AgNO_3$  solution stopper the flask and shake vigorously for 5 minutes If the precipitate is curdy add another 15 ml of alcohol to help break the emulsion Add 3 to 5 ml of ferric alum indicator solution and titrate to an iron red color with the  $NH_4CNS$  solution Shake thoroughly Titrate with the  $AgNO_3$  solution until the iron red color is removed and then back titrate with the  $NH_4CNS$  solution to the reappearance of the iron red color Record the total volume of each solution used in this titration

**NOTE**—The sample taken for analysis should contain 0.001 to 0.01 g of mercaptan sulfur Therefore the size of the sample depends on the mercaptan sulfur content

**Calculation**—Calculate the mercaptan sulfur content of the sample as follows

$$\text{Mercaptan sulfur per cent by weight} = \frac{(V_1 N_1 - V_2 N_2) \times 0.032 \times 100}{W}$$

where  $V_1$  = milliliters of  $AgNO_3$  solution added to the sample

$N_1$  = normality of the  $AgNO_3$  solution

$V_2$  = milliliters of  $NH_4CNS$  solution used for the back titration

$N_2$  = normality of the  $NH_4CNS$  solution and

$W$  = grams of sample used (milliliters of sample multiplied by specific gravity)

**Precision** Duplicate results by the same operator should not be considered suspect unless they differ by more than the following amounts

<i>Mercaptan Sulfur Content Per Cent by Weight</i>	<i>Repeatability</i>
0.0003 to 0.001	0.0001
0.0010 to 0.005	0.0002
0.0050 to 0.010	0.0005

The average of results obtained in different laboratories should not be considered suspect unless the two results differ by more than the following amounts

<i>Mercaptan Sulfur Content, Per Cent by Weight</i>	<i>Reproducibility</i>
0.0003 to 0.001	0.0004
0.0010 to 0.005	0.0006
0.0050 to 0.010	0.0009

LEAD ANTIKNOCK COMPOUNDS IN GASOLINE<sup>35</sup>

This method describes a procedure for the determination of tetraethyllead in gasoline and other volatile distillates.

NOTE.—ASTM Method D1269, Test for Lead Antiknock Compounds in Gasoline, is also available. Both methods give equivalent results within their stated precision limits.

**Outline of Method.**—The lead alkyl is converted to lead chloride and extracted from the gasoline by refluxing with concentrated hydrochloric acid. The acid extract is evaporated to dryness, any organic material present is removed by oxidation with nitric acid, and the lead is determined gravimetrically as lead chromate.

**Apparatus.** Extraction Apparatus, constructed of borosilicate glass,<sup>36</sup> conforming to the dimensions given in Fig. 40-39, and consisting of the following component parts:

Boiling Flask, 500-ml. capacity.

Hopkins Reflex Condenser, having a vapor outlet connected by a rubber tube to an outside vent or to a suction hood.

Thistle Tube, approximately 70-ml. capacity, with a line to indicate approximately the 50-ml. level.

Heating Tube, containing a chimney for increasing convection in the liquid.

Heating Coil, 250-watts, consisting of 9 ft. of No. 30 B & S gage Nichrome wire.

Rheostat, 25-ohms resistance, 2-amp. minimum capacity, for regulating the heater.

Filtering Crucible, 25-ml. porcelain crucibles, having porous bottoms equivalent to Sela's crucible No. 3001,<sup>37</sup> or alternatively 25-ml. Gooch crucibles, capable of retaining a fine precipitate.

**Reagents.**—Unless otherwise indicated, it is intended that all reagents conform to the specifications established by the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. References to water shall be understood to mean lead-free distilled water.

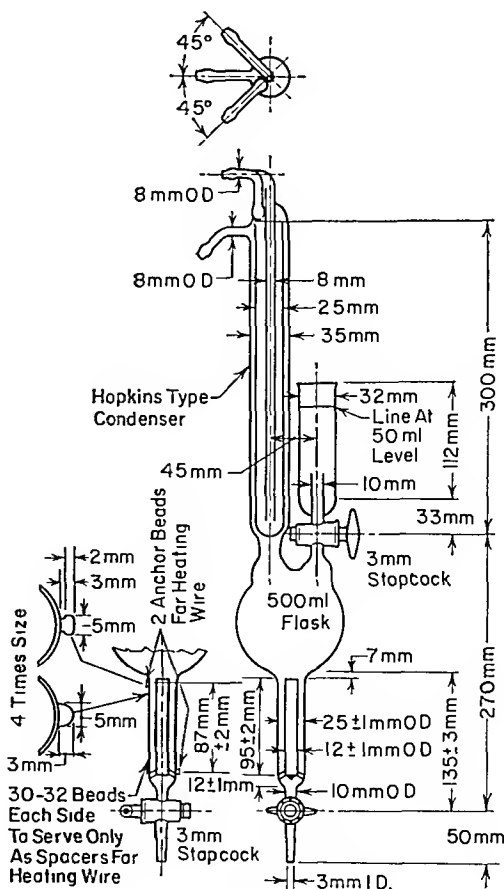


FIG. 40-39. Extraction Apparatus.

<sup>35</sup> Standardized as ASTM D526-61 and ASA No.: Z11.48-1961.

<sup>36</sup> Pyrex glass is satisfactory for this purpose.

<sup>37</sup> Obtainable from Fisher Scientific Co., Pittsburgh, Pa.

## 2010 PETROLEUM AND PETROLEUM PRODUCTS

**Acetic Acid Solution**—Dilute one volume of glacial acetic acid with one volume of water

**Ammonium Hydroxide Solution (1:1)** Dilute one volume of concentrated  $\text{NH}_4\text{OH}$  (sp gr 0.90) with one volume of water

**Asbestos**—Medium fiber acid washed and ignited for use with Gooch crucibles

**NOTE**—Test the asbestos used under the conditions of the analysis to determine its loss in weight due to solubility or to mechanical disintegration. If necessary pick over the asbestos by hand to remove coarse material and then acid wash prior to use.

**Heavy Distillate**—A straight run lead free petroleum distillate of low bromine number with approximately 10% distilling at 400°F and 90% at 460°F

**Hydrochloric Acid** (sp gr 1.19)

**Nitric Acid** (sp gr 1.42)

**Nitric Acid Solution**—Add one volume of concentrated  $\text{HNO}_3$  to 20 volumes of water

**Potassium Chlorate Nitric Acid Solution**—Dissolve 78 g of  $\text{KClO}_3$  in 550 ml of concentrated  $\text{HNO}_3$

**p Nitrophenol Indicator Solution**—Dissolve 0.5 g of p nitrophenol in 100 ml of water and filter if necessary to remove insoluble material

**Potassium Dichromate Solution**—Dissolve 100 g of  $\text{K}_2\text{Cr}_2\text{O}_7$  in 1 liter of water and filter

**Procedure**—Obtain the temperature of the sample of gasoline to be tested to the nearest 1.0°F (NOTE below). Using a pipet<sup>3</sup> transfer a  $50 \pm 0.05$  ml sample of the gasoline to the flask (Fig. 40.39) through the thistle tube and add approximately 50 ml of heavy distillate. Add 50 ml of concentrated HCl and reflux the acid and gasoline for 30 minutes. Use the full heat of the heater until boiling has begun (usually 0.5 to 1 minute) then reduce the heat by regulating the rheostat so that there is at no time a steady stream of condensate from the condenser. After the 30 minute reflux period turn off the heat allow the sample to cool a few minutes and drain the acid layer into a 400 ml beaker. Then add 50 ml of water and reflux the water and gasoline for 5 minutes using the full heat of the heater. Drain the water into the 400 ml beaker and repeat the water extraction.

**NOTE**—For gasolines having a Reid vapor pressure above 7.0 lb the sealed sample container shall be cooled to approximately 60°F (15°C) before removing sample for analysis.

Evaporate the aqueous extract to dryness (NOTE a). Add 3 ml of concentrated  $\text{HNO}_3$  to the residue cover the beaker with a watch glass and heat to oxidize any organic material present (NOTE b). Repeat the  $\text{HNO}_3$  treatment. If a white residue is not obtained after two additions of  $\text{HNO}_3$  oxidize the remaining organic matter with the  $\text{KClO}_3$   $\text{HNO}_3$  mixture as described in NOTE b. Add 4 ml of dilute  $\text{HNO}_3$  mixture and 25 ml of water heat until all the lead salt is in solution.

**NOTE a**—To reduce the evaporation time it is permissible to employ an air jet under the following conditions. Substitute a 500 ml Erlenmeyer flask for the 400 ml beaker evaporate on a hot plate whose surface temperature is maintained between 230 and 250°C while impinging upon the surface of the liquid a stream of hot (about 75°C) clean air at a rate of about 10 l per minute. The air stream should be led into the flask by means of a glass tube with an orifice about 5 mm in diameter placed about 60 mm above the surface of the liquid. The air stream should not be used in the  $\text{HNO}_3$  evaporation.

<sup>3</sup> a Kimble. Norman Kimble Glass Co. Toledo Ohio meets these requirements.

NOTE *b*.—If the residue flashes on being heated with  $\text{HNO}_3$ , the sample should be discarded and the acid extraction repeated on another sample of the gasoline. Then evaporate the extract until crystallization commences, but not to complete dryness. Add 10 ml. of  $\text{KClO}_3\text{-HNO}_3$  mixture, cover the beaker with a watch glass and evaporate the mixture almost to dryness. Repeat this treatment, if necessary, to obtain a white residue.

Cool the sample, add 6 drops of *p*-nitrophenol indicator solution, and add  $\text{NH}_4\text{OH}$  until the indicator changes color, then add approximately 4 to 5 ml. in excess. Add acetic acid to neutralize the  $\text{NH}_4\text{OH}$ , then add 1 to 2 ml. in excess. Filter the solution through a loose-texture filter paper and collect the filtrate in a 600-ml. beaker. Wash the paper with hot water, and dilute the filtrate to 350 to 400 ml. with water. Heat the solution to boiling on a hot plate and add 25 ml. of the  $\text{K}_2\text{Cr}_2\text{O}_7$  solution dropwise from a pipet. Continue boiling until the precipitated  $\text{PbCrO}_4$  is deep orange in color (usually 5 to 7 minutes). Allow the precipitate to settle 3 to 4 hours, or overnight. Filter the sample through a filtering crucible previously dried at 110 to 120°C. and weighed. Wash the beaker and precipitate with hot water, dry the precipitate and crucible in an oven at 110 to 120°C. for 1 hour, cool in a desiccator, and weigh the  $\text{PbCrO}_4$ .

Calculation.—Calculate the concentration of lead by means of one of the following equations:

NOTE.—For gasoline containing only tetraethyllead (TEL) or tetramethyllead (TML), the grams of lead per gallon can be converted to milliliters per gallon. The following equations use the factors 1.561/1.65 and 1.290/1.99 for conversion of TEL and TML from a weight to a volume basis, respectively, where the numerators convert the weight of lead to the respective lead alkyl and the denominators are the density of TEL and TML, respectively:

$$\text{TEL, ml. per gal.} = 0.946A$$

$$\text{TML, ml. per gal.} = 0.648A$$

where  $A$  = g. of lead per gallon at 60°F.

$$\text{Lead, g. per U. S. gal. at 60°F.} = 48.41G[1 + 0.00065(t - 60)]$$

$$\text{Lead, g. per Imperial gal. at 60°F.} = 58.14G[1 + 0.00065(t - 60)]$$

$$\text{Lead, g. per liter at 15°C.} = 12.79G[1 + 0.0012(t_x - 15)]$$

where  $G$  = weight of  $\text{PbCrO}_4$ , in grams,

$t$  = temperature of gasoline when pipeting sample, in degrees Fahrenheit, and

$t_x$  = temperature of gasoline when pipeting sample, in degrees Centigrade.

NOTE.—The constant 48.41 is obtained from the expression  $0.6394 \times 3785.3/50$ , where 0.6394 is an empirical factor for converting  $\text{PbCrO}_4$  to lead, 3785.3 is the number of milliliters in a U. S. gallon, and 50 represents the sample volume in milliliters. The constant 58.14 is obtained by multiplying 48.41 by 1.201 (the ratio of milliliters in an Imperial gallon to milliliters in a U. S. gallon, 4546.0 and 3785.3, respectively). The constant 12.79 is obtained by dividing 48.41 by 3.7853.

NOTE.—The coefficient of expansion of motor gasoline per degree Fahrenheit at 60°F. is 0.0006, and that of aviation gasoline 0.0007. As a reasonable compromise, 0.00065 is selected in the above equations as the factor to apply.

Precision.—The following criteria should be used for judging the acceptability of results (95% probability) when only tetraethyllead is present:

Repeatability.—Duplicate results by the same operator should not be considered suspect unless they differ by more than the following amounts:

$$\text{Repeatability} \dots\dots\dots 0.032 + 0.022A$$

where  $A$  = grams of lead per gallon at 60°F.

## 2012 PETROLEUM AND PETROLEUM PRODUCTS

**Reproducibility**—The results submitted by each of two laboratories should not be considered suspect unless they differ by more than the following amounts

Reproducibility	0.063 + 0.027 <i>A</i>
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where *A* = grams of lead per gallon at 60°F

The following criteria should be used for judging the acceptability of results (95% probability) when tetramethyllead mixtures of tetraethyllead and tetramethyllead or mixtures of other alkyl lead compounds are present

**Repeatability**—Duplicate results by the same operator should not be considered suspect unless they differ from each other by more than the following amount

Repeatability	0.07 g of lead per U. S. gal
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**Reproducibility**—The results submitted by each of two laboratories should not be considered suspect unless they differ by more than the following amount

Reproducibility	0.13 g of lead per U. S. gal
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As an exception to the precision limits given above, the wider limit for repeatability and reproducibility should apply in the analysis of samples in which the antiknock compound is unknown

### SULFUR IN PETROLEUM PRODUCTS BY THE BOMB METHOD <sup>33</sup>

This method describes the procedure for the determination of sulfur in petroleum products including lubricating oils containing additives, additive concentrates and lubricating greases that cannot be burned completely in a wick lamp. The method is applicable to any petroleum product sufficiently low in volatility that it can be weighed accurately in an open sample boat.

**NOTE**—This method is not applicable to samples containing elements that give residues other than barium sulfate which are insoluble in dilute hydrochloric acid solutions and would interfere in the precipitation step. These interfering elements include iron, aluminum, calcium, silicon and lead which are sometimes present in greases, lube oil additives or additive oils. Other acid insoluble materials that interfere are silica, molybdenum disulfide, asbestos, mica, etc. The method is not applicable to used oils containing wear metals and lead or silicates from contamination. Samples that are excluded can be analyzed by ASTM Method D1572.

**Summary of Method**—The sample is oxidized by combustion in a bomb containing oxygen under pressure. The sulfur, as sulfate in the bomb washings, is determined gravimetrically as barium sulfate.

**Safety**—Strict adherence to all of the provisions prescribed hereafter insures against explosive rupture of the bomb, or a blow out, provided the bomb is of proper design and construction and in good mechanical condition. It is desirable, however, that the bomb be enclosed in a shield of steel plate at least 1/2 in. thick or equivalent protection be provided against unforeseeable contingencies.

**Apparatus and Materials**—The apparatus and materials shall consist of the following

<sup>33</sup> Standardized as ASTM D129-60 and ASA No. Z11.110-1961



**Bomb**, having a capacity of not less than 300 ml., so constructed that it will not leak during the test and that quantitative recovery of the liquids from the bomb may be readily achieved. The inner surface of the bomb may be made of stainless steel or any other material that will not be affected by the combustion process or products. Materials used in the bomb assembly, such as the head gasket and lead-wire insulation, shall be resistant to heat and chemical action, and shall not undergo any reaction that will affect the sulfur content of the liquid in the bomb.

**Sample Cup**, platinum, 24 mm. in outside diameter at the bottom, 27 mm. in outside diameter at the top, 12 mm. in height outside, and weighing 10 to 11 g.

**Firing Wire**, platinum, approximately No. 26 B & S gage.

**Caution.**—*The switch in the ignition circuit shall be of a type which remains open, except when held in closed position by the operator.*

**Ignition Circuit**, capable of supplying sufficient current to ignite the cotton wicking or nylon thread without melting the wire.

**Cotton Wicking or Nylon Sewing Thread**, white.

**Reagents.**—Unless otherwise indicated, it is intended that all reagents shall conform to the specifications established by the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available.

**Barium Chloride Solution** (85 g. per l.).—Dissolve 100 g. of  $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$  in distilled water and dilute to 1 liter.

**Bromine Water** (saturated).

**Hydrochloric Acid** (sp. gr. 1.18).

**Oxygen**, free of combustible material and sulfur compounds, available at a pressure of 40 atmospheres.

**Sodium Carbonate Solution** (50 g. per l.).—Dissolve 135 g. of  $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$  or its equivalent weight in distilled water and dilute to 1 liter.

**White Oil**, USP.

**Procedure.** Preparation of Bomb and Sample.—Cut a piece of firing wire 100 mm. in length. Coil the middle section (about 20 mm.) and attach the free ends to the terminals. Arrange the coil so that it will be above and to one side of the sample cup. Insert between two loops of the coil a wisp of cotton or nylon thread of such length that one end will extend into the sample cup. Place about 5 ml. of  $\text{Na}_2\text{CO}_3$  solution in the bomb (NOTE *a*) and rotate the bomb in such a manner that the interior surface is moistened by the solution. Introduce into the sample cup the quantities of sample and white oil (NOTES *b* and *c*) specified in the following table, weighing the sample to the nearest 0.2 mg. (when white oil is used, stir the mixture with a short length of quartz rod and allow the rod to remain in the sample cup during the combustion).

**NOTE a.**—After repeated use of the bomb for sulfur determinations, a film may be noticed on the inner surface. This dullness should be removed by periodic polishing of the bomb. A satisfactory method for doing this is to rotate the bomb in a lathe at about 300 r.p.m. and polish the inside surface with Grit No. 2/0, or equivalent paper,<sup>30</sup> coated with a light machine oil to prevent cutting, and then with a paste of grit-free chromic oxide and water. This procedure will remove all but very deep pits and put a high polish on the surface. Before using the bomb it should be washed with soap and water to remove oil or paste left from the polishing operation.

**Caution.**—*Do not use more than 1 g. total of sample and white oil or other low sulfur combustible material.*

<sup>30</sup> Emery Polishing Paper Grit No. 2/0 may be purchased from the Behr-Manning Co., Troy, N. Y. Chromic oxide may be purchased from J. T. Baker & Co., Phillipsburg, N. J.

Sulfur Content, per cent	Weight of Sample, g	Weight of White Oil, g
5 or under	0.6 to 0.8	0.0
Over 5	0.3 to 0.4	0.3 to 0.4

NOTE b—Use of sample weights containing over 20 mg of chlorine may cause corrosion of the bomb. To avoid this it is recommended that for samples containing over 2% chlorine the sample weight be based on the chlorine content as given in the following table.

Chlorine Content, per cent	Weight of Sample, g	Weight of White Oil, g
2 to 5	0.4	0.4
5 to 10	0.2	0.6
10 to 20	0.1	0.7
20 to 50	0.05	0.7

NOTE c—If the sample is not readily miscible with U.S.P. white oil, some other low sulfur combustible diluent may be employed in place of the white oil. However the combined weight of sample and nonvolatile diluent shall not exceed 1 g.

**Addition of Oxygen**—Place the sample cup in position and arrange the cotton wisp or nylon thread so that the end dips into the sample. Assemble the bomb and tighten the cover securely. *Caution—Do not add oxygen or ignite the sample if the bomb has been jarred, dropped, or tilted.* Admit oxygen slowly (to avoid blowing the oil from the cup) until a pressure is reached as indicated in the following table.

Capacity of Bomb, ml	Minimum Gage Pressure, <sup>a</sup> atmospheres	Maximum Gage Pressure, <sup>a</sup> atmospheres
300 to 350	38	40
350 to 400	35	37
400 to 450	30	32
450 to 500	27	29

<sup>a</sup> The minimum pressures are specified to provide sufficient oxygen for complete combustion and the maximum pressures represent a safety requirement.

**Combustion.**—Immerse the bomb in a cold distilled-water bath. Connect the terminals to the open electrical circuit. Close the circuit to ignite the sample. Remove the bomb from the bath after immersion for at least 10 minutes. Release the pressure at a slow, uniform rate such that the operation requires not less than 1 minute. Open the bomb and examine the contents. If traces of unburned oil or sooty deposits are found, discard the determination and thoroughly clean the bomb before again putting it in use (NOTE *a*).

**Collection of Sulfur Solution.**—Rinse the interior of the bomb, the oil cup, and the inner surface of the bomb cover with a fine jet of distilled water, and collect the washings in a 600-ml. beaker having a mark to indicate 75 ml. Remove any precipitate in the bomb by means of a rubber policeman. Wash the base of the terminals until the washings are neutral to a suitable indicator. Add 10 ml. of saturated bromine water to the washings in the beaker. (The volume of the washings is normally in excess of 300 ml.) Place the sample cup in a 50-ml. beaker. Add 5 ml. of saturated bromine water, 2 ml. of HCl, and enough distilled water just to cover the cup. Heat the contents of the beaker to just below its boiling point for 3 or 4 minutes and add to the beaker containing the bomb washings. Wash the sample cup and the 50-ml. beaker thoroughly with distilled water. Remove any precipitate in the cup by means of a rubber policeman. Add the washings from the cup and the 50-ml. beaker, and the precipitate, if any, to the bomb washings in the 600-ml. beaker. Do not filter any of the washings, since filtering would remove any sulfur present as insoluble material.

**Determination of Sulfur.**—Evaporate the combined washings to 200 ml. on a hot plate or other source of heat. Adjust the heat to maintain slow boiling of the solution and add 10 ml. of BaCl<sub>2</sub> solution, either in a fine stream or dropwise. Stir the solution during the addition and for 2 minutes thereafter. Cover the beaker with a fluted watch glass and continue boiling slowly until the solution has evaporated to a volume of approximately 75 ml. as indicated by a mark on the beaker. Remove the beaker from the hot plate (or other source of heat) and allow it to cool for 1 hour before filtering. Filter the supernatant liquid through an ashless, quantitative filter paper (NOTE *d*). Wash the precipitate with water, first by decantation and then on the filter, until free from chloride. Transfer the paper and precipitate to a weighed crucible and dry (NOTE *e*) at low heat until the moisture has evaporated. Char the paper completely without igniting it, and finally ignite at a bright red heat until the residue is white in color. After ignition is complete, allow the crucible to cool to room temperature, and weigh.

NOTE *d*.—A weighed porcelain filter crucible (Selas type) of 5- to 9- $\mu$  porosity may be used in place of the filter paper. In this case the precipitate is washed free of chloride and then dried to constant weight at  $500 \pm 25^\circ\text{C}$ .

NOTE *e*.—A satisfactory means of drying, charring, and igniting the paper and precipitate is to place the crucible containing the wet filter paper in a cold electric muffle furnace and to turn on the current. Drying, charring, and ignition usually will occur at the desired rate.

**Blank.**—Make a blank determination whenever new reagents, white oil, or other low-sulfur combustible material are used. When running a blank on white oil, use 0.3 to 0.4 g. and follow the normal procedure.

**Calculation.**—Calculate the sulfur content of the sample as follows:

$$\text{Sulfur, per cent by weight} = \frac{(P - B)13.73}{W}$$

where  $P$  = grams of  $\text{BaSO}_4$  obtained from sample,  
 $B$  = grams of  $\text{BaSO}_4$  obtained from blank, and  
 $W$  = grams of sample used

**Precision.**—Duplicate results should not be considered suspect unless they differ by more than the following amounts (NOTE f).

Sulfur, per cent by weight	Repeatability	Reproducibility
0 to 0.5	0.04	0.05
0.5 to 1.0	0.06	0.09
1.0 to 1.5	0.08	0.15
1.5 to 2.0	0.12	0.25
2.0 to 5.0	0.18	0.27

NOTE—The precision shown in the above table does not apply to samples containing over 2% chlorine because an added restriction on the amount of sample which can be ignited is imposed

### DILUTION OF GASOLINE ENGINE CRANKCASE OILS <sup>40</sup>

This method determines the amount of dilution in crankcase oils of engines when gasoline has been used as the fuel

**Outline of Method.**—The sample, mixed with water, is placed in a glass still provided with a reflux condenser discharging into a graduated trap connected to the still. Heat is applied, and the contents of the still are brought to boiling. The diluent in the sample is vaporized with the water and then liquefied in the condenser. The diluent collects at the top of the trap, and the excess water runs back to the still where it is again vaporized, carrying over an additional quantity of diluent. The boiling is continued until all the diluent has been boiled out and recovered in the trap and the volume is recorded.

**Apparatus.** Flask, round bottomed, short necked, having a nominal capacity of 1 liter. Figure 40-40 shows recommended designs and glass connections.

Condenser, Liebig straight type with a jacket not less than 400 mm long, and with an inner tube having an outside diameter of 10 to 13 mm. Figure 40-40 shows characteristic details of suitable condensers.

Trap, in accordance with the details of construction shown in Fig. 40-40 and conforming to the following requirements. It should be graduated from 0 to 5 ml in 0.1 ml divisions. It should be calibrated at four or more points by first filling it with water and then adding Stoddard Solvent from a standard buret having a calibrated capacity at least equal to that of the trap. The Stoddard Solvent should conform to ASTM Specifications D484, Stoddard Solvent. The error of the indicated volume should not exceed 0.05 ml.

Heater.—Any suitable gas burner or electric heater may be used with the glass flask.

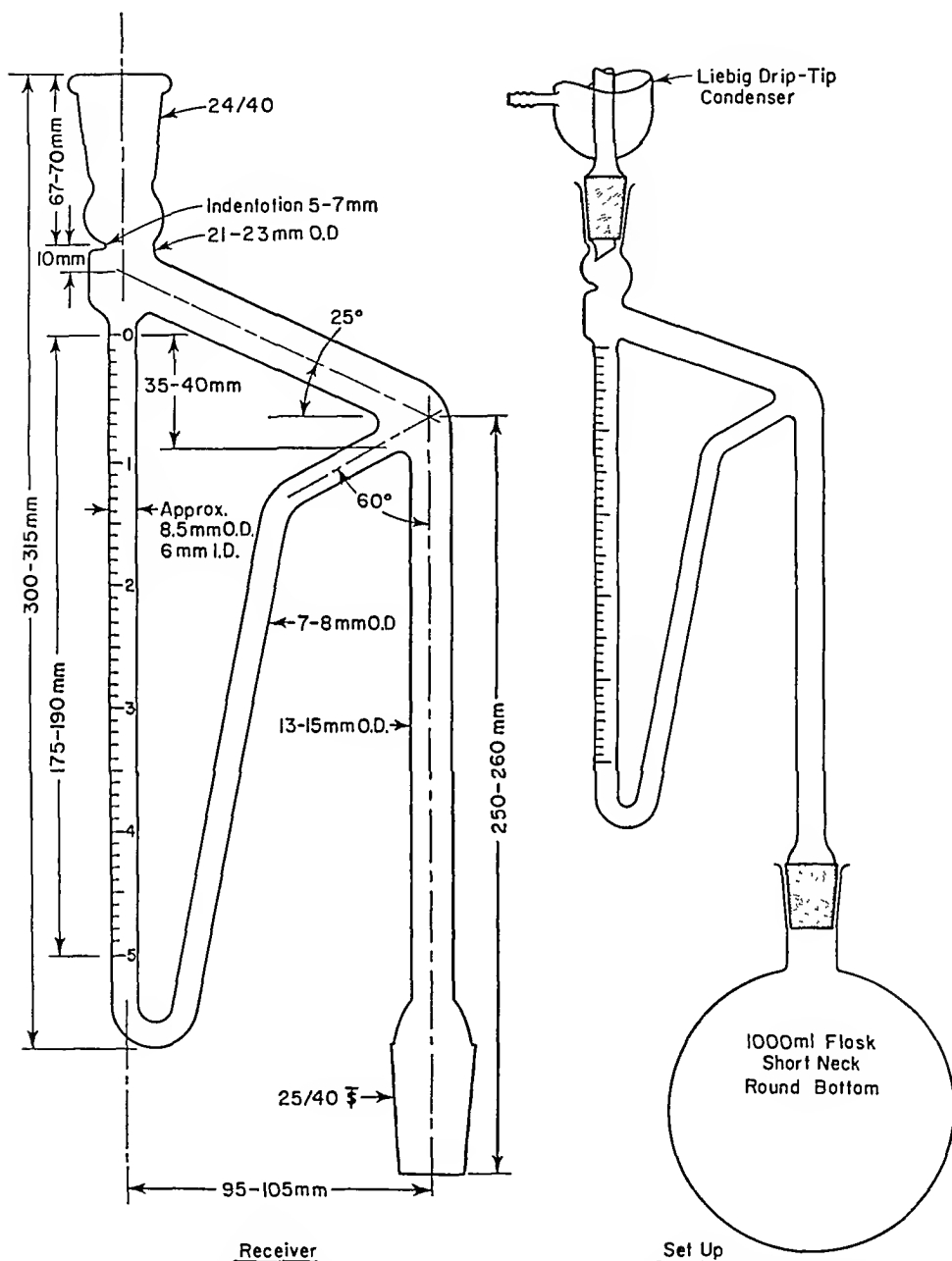


FIG. 40-40. Apparatus for Determining Diluent in Gasoline Engine Crankcase Oil.

**Procedure**—Mix the sample thoroughly, measure 25 ml by means of a 25 ml graduated cylinder, and transfer as much as possible of the contents of the cylinder by pouring it into the flask. Wash the graduated cylinder with successive portions of hot water until only a negligible amount of oil is left in the cylinder. Add additional water to the flask to make a total of approximately 500 ml of water. Fill the trap with cold water and add 1 ml of ethanol to the water in the trap.

Assemble the apparatus as shown in Fig 40 40 so that the tip of the condenser is directly over the indentation in the trap.

Apply heat to the flask at such a rate that refluxing starts within 7 to 10 minutes after heat is applied, with the water and sample being at 70 to 100°F prior to application of heat. After boiling and condensation has commenced adjust the rate of boiling so that condensed distillate is discharged from the condenser at a rate of 1 to 3 drops per second.

**NOTE**—Bumping with a tendency to froth over is often experienced with dirty oils. The use of boiling stones, steel wool or about 5 ml of concentrated hydrochloric acid (HCl) in the flask is often helpful in eliminating this difficulty.

Obtain readings of the amount of diluent at the following times, taken from the time that refluxing starts: 5, 15, and 30 minutes and each 15 minutes following until the test is complete. Completion of the test shall be determined on the basis of either or both of the following criteria:

(1) The test is complete when the volume of diluent increases by not more than 0.1 ml in any 15 minute period during the course of the test.

(2) The test is complete when the volume of diluent obtained in a given time indicates completion, as follows:

Time from Start of Refluxing	Test is Complete if Apparent Volume of Diluent Collected is Equal to or Less Than
5 minutes	No Visible Diluent *
30 minutes	2.0 ml
60 minutes	4.0 ml
90 minutes	5.0 ml

\* Report as "no dilution", otherwise the test should be continued at least 30 minutes.

When the test continues without reaching the limit defined in Paragraph (1), above, to a point at which any of the conditions described in Paragraph (2) above are encountered, the latter should define the completion of the test.

When the test is complete, by either of the criteria defined in Paragraphs (1) and (2), above, turn off the heat. Allow the equipment to stand at least 30 minutes to allow the distillate to settle clear and to cool to approximately room temperature. Read the volume of diluent collected in the trap. If the volume of diluent exceeds the calibrated capacity of the trap, discontinue the test and report the results as 20% plus.

**Calculations.**—The diluent content of the sample, expressed as volume per cent, is equal to the volume of diluent in milliliters multiplied by 4.

**Precision.**—The following data should be used for judging the acceptability of results (95% probability) according to the concept of precision as given in the ASTM Proposed Recommended Practices for Applying Precision Data Given in ASTM Methods of Test for Petroleum Products and Lubricants.

**Reproducibility.**—The results submitted by each of two laboratories should not be considered suspect unless they differ by more than the following amounts:

Diluent Content	Reproducibility
Below 5 per cent.....	2.0
5 per cent and above.....	3.0

**Repeatability.**—Duplicate determinations by the same operator should, in general, show a closer agreement than the reproducibility indicated above.

## SULFUR IN PETROLEUM PRODUCTS INCLUDING LIQUEFIED PETROLEUM GAS BY LAMP COMBUSTION METHOD 1<sup>41</sup>

1(a) This method describes procedures for the determination of total sulfur in liquid petroleum products in concentrations above 0.002% by weight and combined sulfur in liquid petroleum gas or in light hydrocarbon mixtures boiling in this range.

**NOTE.**—The comparable lamp method for the determination of sulfur in fuel gases is described in ASTM Method D1072. For the determination of sulfur in heavier petroleum products that cannot be burned in a lamp, see the bomb method (ASTM D129), the quartz tube method (ASTM D1551), or the high-temperature combustion method (ASTM D1552).

(b) The direct burning procedure (Section 8) is applicable to the analysis of such materials as gasoline, kerosene, naphtha, industrial aromatic hydrocarbons, and other liquids that can be burned completely in a wick lamp. The blending procedure (Section 9) is applicable to the analysis of gas oils and distillate fuel oils, naphthenic acids, alkyl phenols, high sulfur content petroleum products, and many other materials that cannot be burned satisfactorily by the direct burning procedure. The procedure in Section 10 is applicable to liquefied petroleum products such as liquefied petroleum gas, butadiene, and other low-boiling olefin concentrates.

(c) Phosphorus compounds normally present in commercial gasoline do not interfere. A correction is given for the small amount of acid resulting from the combustion of the tetraethyllead antiknock fluids in gasolines. Appreciable concentrations of acid-forming or base-forming elements from other sources interfere when the titration procedure is employed since no correction is provided in these cases.

(d) Elemental sulfur in liquefied petroleum gas is not quantitatively determined by these procedures.

<sup>41</sup> Approved as ASTM D1266-59T and ASA No.: Z11.29-1959.

*Summary of Method—2(a)* The sample is burned in a closed system using a suitable lamp and an artificial atmosphere composed of 70% carbon dioxide and 30% oxygen to prevent formation of nitrogen oxides. The oxides of sulfur are absorbed and oxidized to sulfuric acid by means of hydrogen peroxide solution which is then flushed with air to remove dissolved carbon dioxide. Sulfur as sulfate in the absorbent is determined acidimetrically by titration with standard sodium hydroxide solution or gravimetrically by precipitation as barium sulfate (see Method 2).

(b) Alternatively the sample may be burned in air the sulfur as sulfate in the absorbent being determined by precipitation as barium sulfate for weighing (see Method 2).

**NOTE** In the absence of acid forming or base forming elements other than sulfur results by the volumetric and gravimetric finishes described are equivalent within the limits of precision of the method.

(c) For sulfur contents below 0.002% by weight it is necessary to determine the sulfate content in the absorber solution turbidimetrically as barium sulfate.

*Apparatus—3(a)* Absorbers Chimneys Lamps and Spray Traps—The standard flask and burner is not suitable for burning highly aromatic mixtures without blending as described in Section 9. The flask and burner for aromatic samples permits burning these samples directly without blending and may also be used to burn nonaromatic samples. With this lamp a second port with control valve in the burner manifold is required.

(b) Cotton Wicking—Clean unused uniform twisted white cotton yarn of good quality <sup>41a</sup>. For the burner to burn aromatic samples use long staple fine spun commercial fine grade.

(c) Manifold System consisting of a vacuum manifold with regulating device valves etc (Fig 40-41) and a dual manifold (burner and chimney) supplying a gas mixture of approximately 70% carbon dioxide (CO<sub>2</sub>) and 30% oxygen (O<sub>2</sub>) at regulated pressures. The vacuum manifold shall be connected to a pump of sufficient capacity to permit a steady gas flow of about 3 liters per minute through each absorber and to maintain a constant manifold pressure of approximately 40 cm of water below atmospheric. The gas mixture in the chimney manifold should be maintained at a nearly constant pressure of 1 to 2 cm of water and the burner manifold at approximately 20 cm of water. A suitable arrangement is shown in Fig 40-42 and described below although any similar system may be used. Modifications of the manifold and associated equipment for burning samples in air are shown in Fig 40-44 and described in Method 2 p 2031.

*Apparatus Detail* Flask and Burner for Nonaromatic Samples—A1 A lamp of chemically resistant glass consisting of a 250 ml Erlenmeyer flask and a burner that conforms to the dimensions shown in Fig 40-41 should be used. The burner consists of two concentric glass tubes the external tube having an arm provided with standard taper glass joints for connection with the flask and the chimney. The upper ends of both burner tubes should be polished and should have plane surfaces that are in the same horizontal plane. The burner should have a 1 mm opening near its base to allow equalization of pressure between the chimney and the flask. When connected with the chimney the lamp should be held in position by rubber bands or metal springs stretched between glass hooks on the flask and chimney.

<sup>41a</sup> Lily Rug yarn white 4 strand (2 to 3 mg per cm per strand) manufactured by Lily Mills Shelby N. C. as Article 241 has been found satisfactory for this purpose.



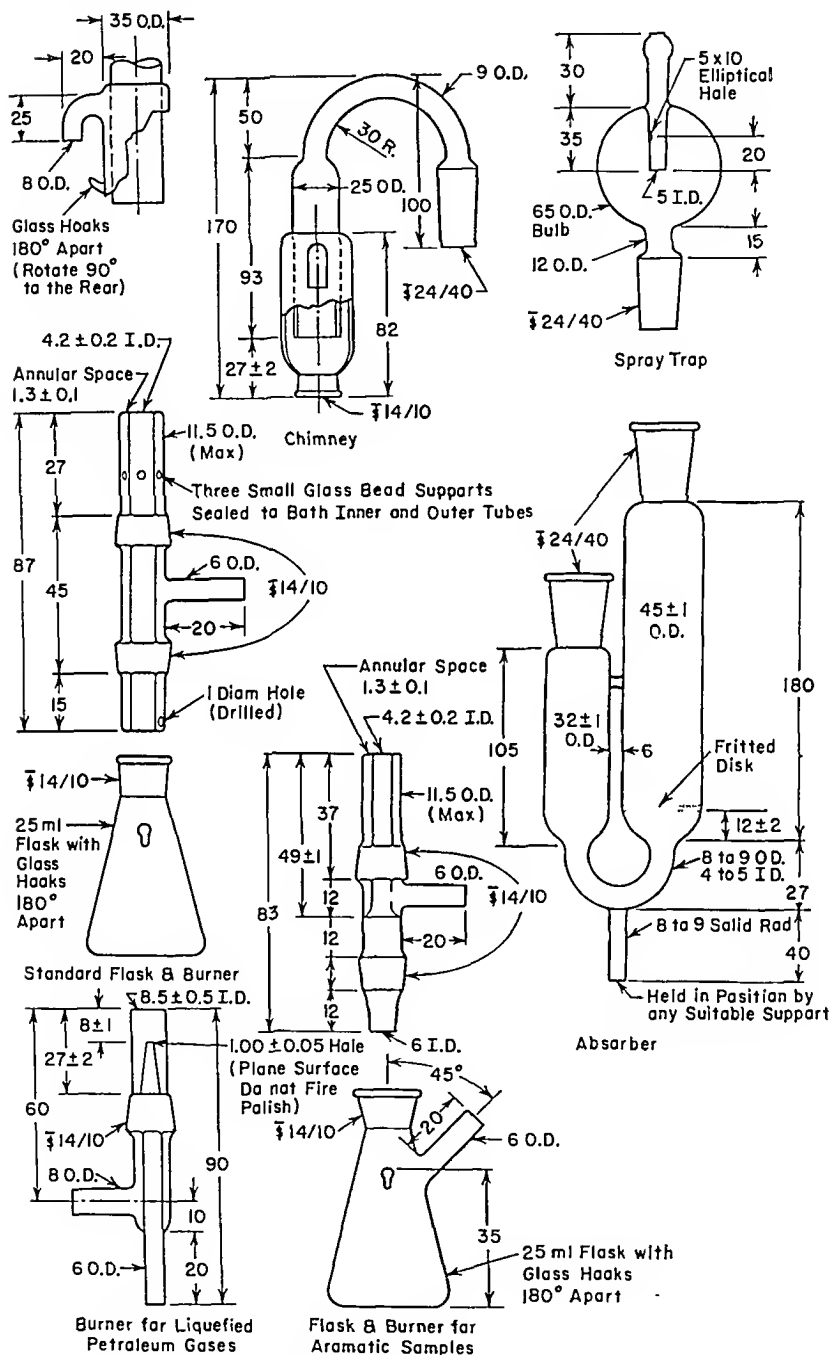


FIG. 40-41. Detailed Drawing of Combustion and Absorption Apparatus. (All Dimensions in Millimeters.)

**Sample Container and Burner for Liquefied Petroleum Gases—A2** The lamp assembly and burner are illustrated in Figs 40 41 and 40 43. The sample vessel should have a capacity of 100 ml and should be made of stainless steel or other corrosion resistant metal.

The sample vessel should be periodically tested at a pressure of 600 psi and should show no measured deformation at this pressure.

**Flask and Burner for Aromatic Samples—A3** A lamp of chemically resistant glass consisting of a 25 ml Erlenmeyer flask with a sidearm and a burner that conforms to the dimensions shown in Fig 40 41, should be used. The burner consists of two concentric glass tubes, the external tube having an arm provided with standard taper glass joints for connecting the burner with the flask and the chimney. The upper ends of both burner tubes should be polished and should have plane surfaces that are in the same horizontal plane. When connected with the chimney the lamps should be held in position by rubber bands or metal springs stretched between glass hooks on the flask and chimney.

**Chimney—A4** A chimney of chemically resistant glass conforming to the dimensions shown in Fig 40 41, provided with standard taper glass joints for connection with the burner and absorber should be used.

**Absorber—A5** An absorber of chemically resistant glass conforming to the dimensions shown in Fig 40 41, provided with standard taper glass joints for connection with the chimney and spray trap should be used. A fritted disk with average pore diameter from 150 to 200  $\mu$  should be sealed in the larger of two bulbs of the absorber. The fritted disk should be of such a porosity that when 50 ml of water is placed in the absorber and air is passed through at the rate of 30 liters per minute in the forward direction the pressure differential between the two sides of the absorber is between 15 and 23 cm of water and the air is dispersed uniformly.

**Spray Trap—A6** A spray trap of chemically resistant glass conforming to the dimensions shown in Fig 40 41, provided with a standard taper glass joint for connection with the absorber should be used.

**Manifold System—A7** A satisfactory vacuum and combustion atmosphere manifold and supply system for supplying the required  $\text{CO}_2$ - $\text{O}_2$  mixture to the lamp assemblies is shown diagrammatically in Fig 40 42. The gases are supplied from commercial cylinders the pressure of each gas being adjusted to  $10 \pm 2$  psig by means of two single stage regulating valves to insure constant pressure at the flow regulating needle valves. It is necessary to pass the  $\text{CO}$  through a heat exchanger installed ahead of the regulating valves to prevent freezing of the valves. The gases are passed through a metering system consisting of two calibrated rotameter flow meters to indicate the proportion of the two gases mixed in the surge tank. Any number of lamp assemblies can be operated as a unit the throughput of the flow meters being chosen accordingly. The tubing that connects the chimney manifold to the chimneys should have an internal diameter not smaller than  $\frac{1}{4}$  in in order to prevent unnecessary restriction in gas flow. The scrubber should have a capacity of about 1 liter.

**Purity of Reagents—4(a)** Reagent grade chemicals should be used in all tests. Unless otherwise indicated it is intended that all reagents should conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society where such specifications are available. Other grades may be used provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without affecting the accuracy of the determination.

(b) Unless otherwise indicated, all references to water shall be understood to mean distilled water.

**Reagents and Materials.** 5(a) Carbon Dioxide and Oxygen.—The carbon dioxide ( $\text{CO}_2$ ) and the oxygen ( $\text{O}_2$ ) should each be at least 99.5% pure. These gases should meet the requirements of Section 8(e).

(b) Diluent.—The diluent used should have a sulfur content less than 0.001%, be completely miscible with the sample to be analyzed, and permit burning at a moderate rate without smoking. *n*-Heptane, isooctane, and absolute ethyl alcohol have been found suitable.

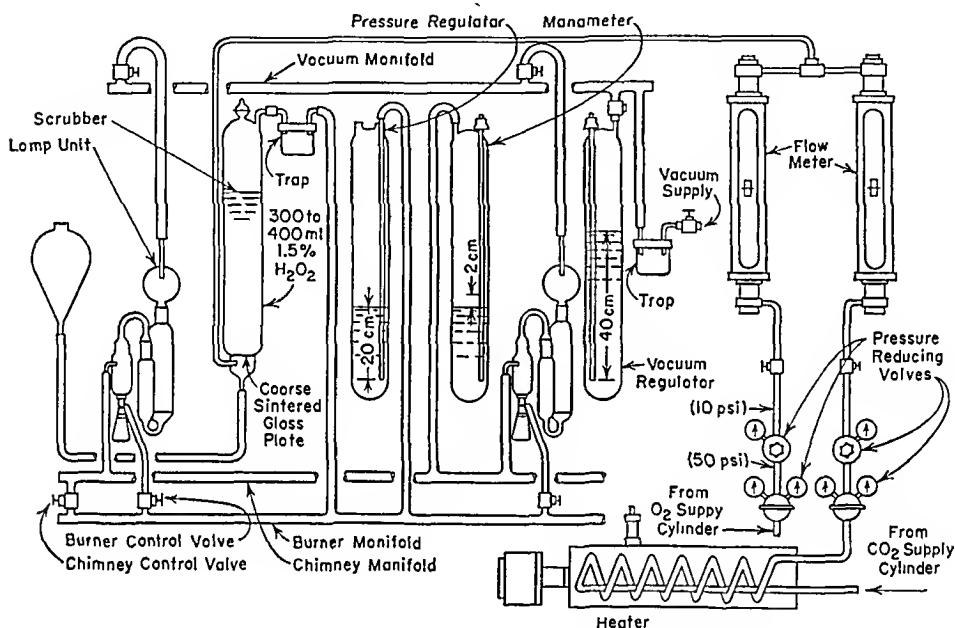


FIG. 40-42. Schematic Diagram of  $\text{CO}_2$ - $\text{O}_2$  Supply Manifold and Lamp System.

(c) Hydrochloric Acid (1:10).—Mix 1 volume of concentrated hydrochloric acid ( $\text{HCl}$ , sp. gr. 1.19) with 10 volumes of water.

(d) Hydrogen Peroxide Solution (1.5%).—Mix 1 volume of hydrogen peroxide ( $\text{H}_2\text{O}_2$ , 30%) with 19 volumes of water. Store in a dark-colored glass-stoppered bottle.

(e) Methyl Purple Indicator.—Aqueous solution containing approximately 0.1% active constituent.<sup>42</sup> (Not methyl violet.)

(f) Sodium Hydroxide Solution (100 g. per liter).—Dissolve 100 g. of sodium hydroxide ( $\text{NaOH}$ ) in water and dilute to 1 liter.

(g) Sodium Hydroxide Standard Solution (0.05 N).—Dilute 2.8 ml. of saturated  $\text{NaOH}$  solution to 1 liter (NOTE), using for this purpose the clear saturated solution decanted after standing long enough to permit any precipitate to settle out. Standardize by titration against standard acid, using the methyl purple indicator.

<sup>42</sup> Fleisher Methyl Purple Indicator, U. S. Patent No. 2416619 may be obtained from Fleisher Chemical Co., Benjamin Franklin Station, Washington 4, D. C., or from any chemical supply company handling Fleisher Methyl Purple.

Store in an alkali resistant glass bottle and protect to minimize contamination by  $\text{CO}_2$  from the air. Use only pure gum rubber tubing for connections between the storage bottles and burets.

**NOTE**—The calculation of results may be simplified by adjusting the normality of the  $\text{NaOH}$  solution to  $0.0624 = 0.0001$ . Then 1 ml of the  $\text{NaOH}$  solution will be equivalent to 0.0010 g of sulfur. In this case the factor 16.03  $\lambda$  in the calculation (Section 12(a)) becomes 1.000.

**Preparation of Apparatus—6(a)** When the apparatus is first assembled charge the absorber with  $30 \pm 2$  ml of water. Adjust the individual valves between the vacuum manifold and spray traps so that approximately 3 l of air per minute will be drawn through each absorber when the chimney outlets are open to the atmosphere while maintaining the pressure in the vacuum manifold at approximately 40 cm of water below atmospheric. When all adjustments have been made remove the water from the absorbers. The height of the liquids in the pressure and vacuum regulators is indicated in Fig. 40.42 and during operation a slow leak of gas through them should be maintained (**NOTE**).

**NOTE** In use place 300 to 400 ml of  $\text{H}_2\text{O}$  solution (1.5%) in the scrubber. Since the manifold manometer also serves as a scrubber at the end of the test to remove  $\text{CO}$  from the absorbent use  $\text{H}_2\text{O}$  solution (1.5%) as the manometric liquid. Replace weekly or whenever the volume becomes appreciably less than the original.

(b) Neutralize the  $\text{H}_2\text{O}$  solution (1.5%) immediately before use. As 30 ml of the solution is needed transfer to a beaker multiples of 30 ml sufficient for the number of absorbers to be used simultaneously. Add 1 drop of methyl purple indicator solution for each 100 ml of  $\text{H}_2\text{O}$  solution and then add 0.05  $\lambda$   $\text{NaOH}$  solution dropwise until the color changes from purple to light green.

(c) Introduce  $30 \pm 2$  ml of the freshly neutralized  $\text{H}_2\text{O}$  solution (1.5%) into the larger bulb of each absorber. In addition for each set of samples burned prepare an extra absorber for use as a control blank. Attach the spray traps and chimneys and connect them to their respective manifolds by means of sulfur-free rubber tubing. Close the chimney openings by means of corks.

(d) With the burner control valves closed the valve to the vacuum regulator fully open and the pressure in the vacuum manifold adjusted to approximately 40 cm of water below atmospheric turn on the  $\text{CO}_2$  and  $\text{O}_2$  supplies (**Caution** see **NOTE a**). Adjust the chimney manifold control valve so that at the required rate of flow through the absorbers only a small stream of  $\text{CO}_2$  gas escapes at the pressure regulator a small stream of air enters at the vacuum regulator and the pressure in the chimney manifold is 1 to 2 cm of water. Minor adjustment of the vacuum regulator and vacuum control valve may be necessary to achieve this condition (**NOTE b**).

**NOTE a Caution**—A hazardous (explosive) condition may result if the  $\text{CO}_2$  supply is interrupted and the  $\text{O}_2$  flow is continued while samples are being burned. The installation of suitable warning or control equipment is recommended.

**NOTE b**—It is convenient to balance the gas flow system by regulating the pressure in the vacuum manifold. This is done by raising or lowering the air inlet tube in the vacuum regulator by sliding it in a rubber sleeve.

(e) Cut the wicking to 30 cm lengths. Use the number of lengths dictated by the sample (see Section 7). Fold the wicking once to give a 15 cm long bundle for threading the burners. Thread the required number of burners by inserting the

looped ends into the top of the inner tube of the burner. Draw the wicking through by means of a metal hook. Trim the wick as close as possible to the top of the burner with a pair of sharp scissors. It is essential that thoroughly cleaned burners and new wicking be used for each test.

**Control of Combustion.**—7(a) Most types of liquid samples burn with a luminous yellow flame, the size and shape of which is dependent on the gas flow to the burner, the volatility of the material, the tightness of the fit of the wick in the burner tube, and the position of the top of the wick relative to the top of the burner. It is preferable that the latter two variables be fixed with relation to the first before burning is started so that the flame can be controlled by variation in the rate of  $\text{CO}_2\text{-O}_2$  flow.

(b) Highly volatile samples require a tight-fitting wick, the top of which may need to be several millimeters below the top of the burner, and in extreme cases may have to be cooled in ice during the burning. Less volatile materials require a more loosely fitting wick and may require warming.

(c) After trimming, draw the wick down until the trimmed edge is flush with or just a little below the top of the burner. With the burner for aromatic samples, the distance from the top of the burner to the top of the wicking should be 8 mm. or more for benzene and 4 mm. for toluene; a slight heating of the upper end of the burner will be helpful in starting vaporization of heavier materials.

(d) To use the standard lamp, light the wick and then slowly admit combustion atmosphere to the burner to obtain a smoke-free flame. To use the burner for aromatic samples, introduce a small amount of combustion atmosphere into the flask to provide sufficient vapor for lighting the burner. After lighting the burner, introduce combustion atmosphere directly into the burner to prevent smoking and to adjust the flame size. If the flame is accidentally snuffed out, relight.

(e) A short burning period (1 to 2 minutes is usually sufficient) at low flame height is necessary to allow combustion to reach equilibrium before the flame size can be increased without causing a smoky flame. In adjusting the standard lamp, the entire control is at the burner. For the burner for aromatic samples, first adjust the flow of gas to the flask and then reduce the flow of gas to the burner as required. In any case, it is essential that the flame burn smoothly and symmetrically and without jets in the inner cone or smoke on the outer fringes.

(f) Satisfactory combustion of materials difficult to burn can sometimes be obtained by increasing the  $\text{O}_2$  content of the combustion atmosphere. Never increase the  $\text{O}_2$  content of the combustion atmosphere to more than 40%.

(g) Before extinguishing the flames, the samples shall be burned until the flask and wicking appear to be dry and the flame has reduced considerably in size; frequently the flame continues to burn a short time after the flask appears dry because of the sample in the wick. For example, for gasoline samples, which burn with a high flame, the flame should be extinguished when it is only 3 to 4 mm. high. If the flame is permitted to burn until it goes out, partially oxidized substances (probably organic acids) are produced; as a result broad, indistinct end points are obtained. When samples are not burned until the flask is apparently dry, erratic results may be obtained. In the case of volatile samples, any unburned sample will escape from the burner during weighing. When elemental sulfur is present, it is particularly important that the sample be burned to apparent dryness and that the wick be maintained flush with the top of the burner to insure complete combustion. With mixtures containing light and heavy hydrocarbons, the more

volatile materials seem to burn first, possibly concentrating sulfur compounds in the material remaining behind

*Procedure for Direct Combustion of Liquid Samples (see also Method 2, p 2031)*

—8(a) By means of an appropriate pipet, introduce into the flask of each lamp an approximate quantity of sample as indicated in Table 40-24 Stopper the flasks

TABLE 40-24 SAMPLE SIZE FOR DIRECT COMBUSTION OF LIQUID SAMPLES

Sulfur Content, per cent by weight	Sample Size	
	g	ml
Under 0.05	10 to 15	20
0.05 to 0.3	5 to 10	10
0.3 to 1	3 to 5	5
Over 1	2 to 3	3

with clean, numbered corks Weigh each flask and its burner to the nearest 0.005 g (NOTE)

NOTE—While the stoppered flasks and prepared burners may all be weighed separately, it is usually more convenient to place each flask and its burner on the balance pan and obtain the combined weight in a single weighing

(b) Handling each lamp individually insert the burner in the flask As soon as the sample has risen by capillary action to the top of the wick connect the side tube of the burner to the burner manifold by means of sulfur free rubber tubing Light the burner with a sulfur free flame (such as an alcohol lamp) and insert into the chimney pinching off the connection between the chimney and the chimney manifold during the insertion if the flame tends to be blown out At the same time adjust the gas flow to the burner so that the flame is maintained at a point just below smoking and has a steady symmetrical appearance Continue in this manner until all lamps have been placed in the chimneys Make any minor adjustment of the chimney manifold control valve necessary to maintain the required pressure (see Section 6) During the burning, and particularly during the latter stages when the flame becomes small decrease the  $\text{CO}_2$   $\text{O}_2$  supply to the burners in order to prevent extinction of the flames (NOTE below)

NOTE—When incomplete combustion occurs the absorber liquid will foam excessively

(c) When the burning of each sample is complete as evidenced by the flame becoming small owing to depletion of the sample remove the burner and flask from the chimney, extinguish the flame shut off the  $\text{CO}_2$   $\text{O}_2$  supply to the burner and stopper the chimney opening Immediately reweigh the flask, burner, and numbered cork When all combustions have been completed, turn off the  $\text{CO}_2$  and the  $\text{O}_2$  supplies, close the chimney control valve, and close the connection to the vacuum regulator, this will cause air to be drawn into the chimney manifold through the manometer Allow air to be drawn through the absorbers in this

manner for 5 minutes to remove dissolved  $\text{CO}_2$  from the absorbent; then close the vacuum control valve (NOTE).

NOTE.—If it is desired to conserve the combustion atmosphere, the gas flow through each individual absorber may be turned off upon completion of the burning period. To accomplish this, pinch off the rubber tubing connecting the spray trap to the vacuum manifold, reduce the flow of mixed gases at the rotameters proportionately, and readjust the vacuum control valve and the chimney control valve. When the burning of all samples has been completed, it is necessary to remove the pinch clamps and readjust the vacuum control valve in order to draw air at the required rate through the absorbers for removal of dissolved  $\text{CO}_2$ .

(d) Rinse the chimneys and spray traps three times, using about 10 ml. of water each time. When the sample contains tetraethyllead, use hot water to rinse the chimneys. Add the rinsings to the absorbers, and titrate as directed in Section 11.

(e) Blank.—Leave the chimney of the blank absorber (Section 6(c)) stoppered, and allow the  $\text{CO}_2\text{-O}_2$  stream to pass through that absorber until all samples started at one time have finished burning. Turn off the  $\text{CO}_2$  and the  $\text{O}_2$  supplies and aerate the blank absorber in the same manner as the sample absorbers (Paragraph 8(c) above). Titrate the absorber liquid as directed in Section 11. Normally, the combustion atmosphere blank will be small, but if the titration requires more than 0.1 ml. of 0.05 *N* NaOH solution discard the determination and replace the  $\text{CO}_2$  cylinder.

*Procedure for Blending and Combustion of Liquid Samples.*—9(a) Add 6 ml. of sulfur-free diluent to each flask. Stopper the flasks with numbered corks and weigh to the nearest 0.005 g. By means of a pipet, introduce into the flask of each burner an approximate quantity of sample as indicated in Table 40-25; swirl to mix thoroughly, and reweigh (NOTE).

TABLE 40-25. SAMPLE SIZE FOR TESTING BLENDED LIQUID SAMPLES

Sulfur Content, per cent by weight	Sample Size	
	g.	ml.
0.5 and under.....	3 to 4	5
Over 0.5.....	2 to 3	3

NOTE.—Alternatively, make a quantitative 40% blend of the sample in sulfur-free diluent and proceed as described in Section 8.

(b) Insert the burner and burn as described in Section 8(b). Remove each lamp from its chimney as the flame nears extinction and extinguish the flame. Add 2 ml. of diluent, allowing the diluent to rinse down the walls of the flask. Burn the additional diluent and repeat the addition of diluent and burning one more time so that a total of 10 ml. of diluent has been burned (NOTE).

NOTE.—In this case, it is desirable that a 10-ml. diluent blank be run; the titration of the absorber solution from this blank shall not exceed 0.1 ml. of 0.05 *N* NaOH solution.

(c) After all lamps have completed burning turn off the  $\text{CO}_2$  and  $\text{O}_2$  supplies close the connection to the vacuum regulator draw air through the absorbers for 5 minutes and finally close the vacuum control valve. Rinse the chimneys and spray traps three times using about 10 ml of water each time. Add the rinsings to the absorbers and titrate as directed in Section 11.

**Procedure for Combustion of Liquefied Petroleum Gases—10(a)** Obtain the sample in a container by the method conforming to the recommendations in ASTM Method D1265 Method of Sampling Liquefied Petroleum Gases.

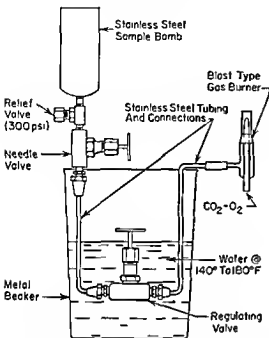


FIG. 40-43 Diagrammatic Sketch of the Liquefied Petroleum Gas Burner Assembly

slightly on the sample container and allow a small amount of the sample to bleed from the loose connection at the metal vessel thereby purging the transfer line (*Caution* see NOTE below). Take care to exclude all air when filling the metal vessel because hydrogen sulfide ( $\text{H}_2\text{S}$ ) oxidizes rapidly in the presence of metals. Tighten the connection at the metal vessel and introduce 30 to 50 g of the liquid phase of the sample into the evacuated metal vessel.

**NOTE Caution**—If this sample transfer is made in a building observe all necessary fire precautions.

(d) Immediately disconnect the metal vessel and bleed off the liquid phase of the sample until the net weight in the 100 ml metal vessel is 30 to 40 g (*Caution* see NOTE below).

**NOTE Caution**—It is important not to keep the sample vessel liquid full because further liquid expansion on increase of temperature could rupture the vessel.

(e) Weigh the vessel containing the sample to the nearest 0.1 g. Support the sample vessel in an inverted position so that the sample is taken from the liquid phase. Connect the sample vessel to the auxiliary stainless steel regulating valve.

(b) Clean and dry a 100 ml corrosion resistant metal vessel. Remove the needle valve. Wash the interior of the vessel and needle valve, first with a sulfur free hydrocarbon such as n-pentane and then with acetone. Dry the interior of the vessel with clean compressed air and rinse it with HCl (1:10). Rinse the interior with water and then rinse it with NaOH solution (100 g per liter). Rinse the interior of the vessel with water until the wash water is neutral to a pH test paper. Wash the vessel with acetone and allow it to drain for at least 10 minutes. Dry the vessel with a stream of clean compressed air and reassemble.

(c) Evacuate the clean dried metal vessel and connect it to the liquid line of the sample container by means of a short length of stainless steel tubing leaving the connection to the metal vessel somewhat loose. Open the valve



by means of stainless steel tubing (Fig. 40-43) (NOTE below). By means of short lengths of sulfur-free rubber tubing, connect the auxiliary valve outlet to the side inlet of the gas burner and the lower inlet of the gas burner (Section A2, p. 2022) to the burner manifold.

NOTE.—With some samples it may become necessary, for steady burning, to surround the auxiliary valve with a heat-exchanger system. A convenient means is winding insulated heating wire, having a resistance of 40 to 60 ohms, around the auxiliary valve and connecting it to a suitable rheostat. Another means is to place the regulating valve in a suitable metal beaker and cover the valve body with water maintained at 140 to 180°F.

(f) Open the valve on the sample vessel; then open the auxiliary valve to allow a small stream of vapor to escape. Quickly light the burner with a sulfur-free flame. Adjust the flow of  $\text{CO}_2\text{-O}_2$  mixture and sample so that the flame is approximately 35 mm. high and clear blue in color; this color is reached just beyond the point at which a yellow color shows at the tip of the flame. Insert the burner into the chimney and readjust the flame if necessary. Burn approximately the quantity of sample prescribed in Table 40-26. Close the valve on the sample vessel and

TABLE 40-26. SAMPLE SIZE FOR TESTING LIQUEFIED PETROLEUM GASES

Sulfur Content, grains per 100 cu. ft. at 60° F. and 29.92 in. Hg	Sample Size, g.
1 to 5.....	35 to 40
5 to 15.....	10 to 15
Over 15.....	5 to 10

allow the sample contained between this valve and the auxiliary valve to be vaporized and burned. Disconnect the heated auxiliary valve and reweigh the sample vessel to the nearest 0.1 g.

(g) When the combustions have been completed, turn off the  $\text{CO}_2$  and  $\text{O}_2$  supplies, remove the burner from the chimney, close the valve to the vacuum regulator, draw air through the absorbers for 5 minutes, and finally close the vacuum control valve. Rinse the chimneys and spray traps three times, using about 10 ml. of water each time. Add the rinsings to the absorbers and titrate as directed in Section 11.

**Titration of Absorbent Solution.**—11. Add 3 to 4 drops of methyl purple indicator solution to the liquid in each absorber. Titrate the absorbent solution by introducing 0.05 N NaOH solution from a buret into the smaller bulb of the absorber. Use a 10-ml. microburet if less than 10 mg. of sulfur is expected to be present in the absorber. Stir during the titration by applying suction intermittently to the top of the larger bulb (NOTE).

NOTE.—When incomplete combustion of the sample occurs, the air drawn through the absorber during the titration will have a characteristic taste or odor and the end point will be broad. In these cases, discard the determination.

## 2030 PETROLEUM AND PETROLEUM PRODUCTS

Calculations—12(a) Calculate the sulfur content of liquid samples as follows

$$\text{Sulfur content per cent by weight} = 16.03 N \times \frac{A}{10W}$$

where  $A$  = milliliters of NaOH solution required to titrate the acid in the absorbent solution from the burned sample,

$N$  = normality of the NaOH solution (see NOTE), and

$W$  = grams of sample burned

(b) When it is required by specifications to correct the sulfur content (NOTE below) for tetraethyllead fluids calculate the corrected values as follows

$$\text{Corrected sulfur content, per cent by weight} = S - LF$$

where  $F$  = 0.0016 if the sample contains aviation tetraethyllead fluid and 0.0037 if it contains motor tetraethyllead fluid,

$L$  = tetraethyllead content in milliliters per U. S. gallon and

$S$  = sulfur content in per cent by weight

NOTE—These corrections are based on experiments of burning fuels blended with anti-knock fluid containing tetraethyllead and ethylene halide in commonly used combinations

(c) Calculate the sulfur content of liquefied petroleum gases as follows

$$R \text{ (for propane)} = 814S$$

$$R \text{ (for butane)} = 1072S$$

$$R \text{ (for propane butane mixtures)} = S(3374(G - 0.5077) + 814)$$

where  $R$  = grains of total sulfur per 100 cu. ft. of gas at 60°F. and 29.92 in. of mercury,

$S$  = sulfur content in per cent by weight, and

$G$  = specific gravity of the mixture at 60/60°F. (NOTE)

NOTE—If the specific gravity of the mixture is not known determine it by ASTM Method D1657 Test for Specific Gravity of Light Hydrocarbons by Pressure Hydrometer

Precision—13 The following data should be used for judging the acceptability of results (95% probability) as applied to the direct burning of liquid samples in the range of 0.01 per cent to 0.4 per cent sulfur (NOTE below)

(a) *Repeatability*—Duplicate results by the same operator should not be considered suspect unless they differ by more than the following amounts

	<i>Repeatability</i>
Sulfur content	0.005

(b) *Reproducibility*—The results submitted by each of two laboratories should not be considered suspect unless the two results differ by more than the following amounts

	<i>Reproducibility</i>
Sulfur content	0.010 + 0.025S

where  $S$  = the total sulfur content, % by weight, of the sample

NOTE—Test data applicable to liquefied petroleum gas samples are being collected

# SULFUR IN PETROLEUM PRODUCTS BY LAMP COMBUSTION METHOD 2

## AIR BURNING OF SAMPLE. GRAVIMETRIC FINISH

(Abstracted from former ASTM Method D90-55T)

1. This procedure is recommended only for analyzing liquid petroleum samples that can be burned with a wick lamp; it is not recommended for analysis of liquefied petroleum gas samples.

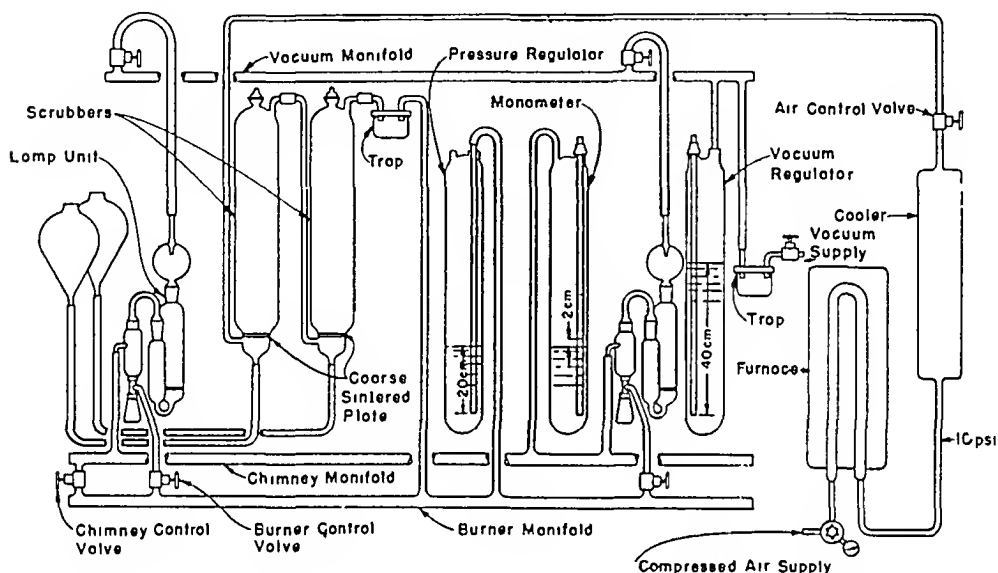


FIG. 40-44. Schematic Diagram of Purified Air Supply Manifold and Lamp System.

*Apparatus.*—2. The manifold system described in Section 3(c) may be used with only a slight modification. Filtered air should be substituted for the  $\text{CO}_2\text{-O}_2$  supply train and a second sintered-plate scrubber should be added to the incoming air line as shown in Fig. 40-44.

*Additional Reagents.* (See p. 2023 for other reagents.) 3. Barium Chloride Solution (100 g. per liter).—Dissolve 100 g. of barium chloride dihydrate ( $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$ ) in water and dilute to 1 liter.

Hydrochloric Acid (sp. gr. 1.19).—Concentrated hydrochloric acid ( $\text{HCl}$ ).

Hydrogen Peroxide Solution (30%).—Concentrated hydrogen peroxide ( $\text{H}_2\text{O}_2$ ).

Sodium Hydroxide Solution (100 g. per liter).—Dissolve 100 g. of technical grade sodium hydroxide ( $\text{NaOH}$ ) pellets in water and dilute to 1 liter.

Sulfuric Acid (1:16).—Mix 60 ml. of concentrated sulfuric acid ( $\text{H}_2\text{SO}_4$ , sp. gr. 1.84) with 960 ml. of water.

*Preparation of Apparatus.*—4. Place 300 to 400 ml. of  $\text{NaOH}$  solution in the first scrubber (Fig. 40-44) and the same amount of  $\text{H}_2\text{O}_2\text{-H}_2\text{SO}_4$  solution (300 ml. of  $\text{H}_2\text{O}$ , 30 ml. of  $\text{H}_2\text{SO}_4$  (1:16), and 30 ml. of  $\text{H}_2\text{O}_2$  (30%)) in the second scrubber.

For apparatus in daily use replace these solutions two times each week or when ever the volume becomes less than two thirds of the original

Make other preparations as described in Section 6 except that the  $H_2O_2$  solution (1.5%) need not be neutralized

**Procedure for Combustion**—5 Burn the sample as described in Section 8 of Method 1 controlling combustion as described in Section 7 of Method 1 Use a sample size as prescribed in Table 40-27 Analyze the absorber solutions from the samples and blank as described in section following

TABLE 40-27 SAMPLE SIZE FOR AIR BURNING OF LIQUID SAMPLES

Sulfur Content, per cent by weight	Sample Size	
	g	ml
0.5 and under	5 to 10	10
Over 0.5	3 to 5	5

**Procedure for Analysis of Absorber Solutions**—6(a) Transfer the absorber liquid to a 400 ml beaker. Rinse the absorber and chimney thoroughly with water and add the rinsings to the beaker. Filter the solution to remove any foreign material receiving the filtrate in a 400 ml beaker having a mark to indicate 75 ml. Add 2 ml of HCl heat to boiling and add 10 ml of  $BaCl_2$  solution either in a fine stream or dropwise. Stir the solution during the addition and for 2 minutes thereafter.

(b) Cover the beaker with a fluted watch glass and continue boiling slowly until the solution has evaporated to a volume of approximately 75 ml as indicated by the mark on the beaker. Remove the beaker from the hot plate (or other source of heat) and allow to cool 1 hr before filtering.

(c) Filter the supernatant liquid through a close texture ashless filter paper. Wash the precipitate with water first by decantation and then on the filter paper until free of chloride ion. Transfer the paper and precipitate to a suitable weighed crucible and dry at low heat until the moisture has evaporated. Char the paper completely without igniting it and finally ignite at a bright red heat until the precipitate is burned white (NOTE) After ignition is complete allow the crucible to cool to room temperature and weigh.

NOTE: A satisfactory means of accomplishing these operations is to place the uncovered crucible containing the wet filter paper in a cold electric muffle furnace and turn on the current. Drying charring and ignition usually occur at the desired rate.

**Calculation**—7 Calculate the sulfur content of the sample as follows

$$\text{Sulfur content, per cent by weight} = \frac{(w - b) \times 13.73}{W}$$

where  $w$  = grams of barium sulfate ( $\text{BaSO}_4$ ) precipitate in the absorber solution from the burned sample,

$b$  = grams of  $\text{BaSO}_4$  precipitate from the corresponding blank absorber solution (NOTE), and

$W$  = grams of sample burned.

NOTE.—The determination should be discarded if the blank correction used in the calculation exceeds 1.5 mg. of  $\text{BaSO}_4$ . Frequently, impure reagents are the cause of this difficulty.

Precision.—See Section 13 of Method 1, p. 2030, for recommended data.

and boiling points, functional groups, molecular weight, empirical formula, and the arrangement of the molecules in the solid state. Such data are inadequate for characterizing plastics, however. Plastics do not exhibit sharp melting points, but soften gradually with increasing temperature, and finally become more or less viscous liquids. The thermosetting plastics become infusible after an initial heating and decompose on any further increase in temperature. Most plastics are not homogeneous, but are heterogenous mixtures of molecules of similar structure but of different molecular weights. The individual structural unit in a polymer is termed a "mer." The mer has a definite structure and chemical composition, and a molecular weight called the mer weight. Therefore, the molecular weight of the polymer is the product of the mer weight and the number of mer units in the molecule. Conversely, the degree of polymerization (D.P.) is the number of mers in the molecule, and is calculated by dividing the molecular weight by the mer weight.

Some of the molecular characteristics of greatest significance for understanding the physical properties of high polymers are considered to be the nature of the monomer units, molecular weight and molecular weight distribution, and details of chain structure.<sup>2</sup> In addition to defining the molecular characteristics of the plastic, it is usually necessary also to determine the intentional and unintentional additives.

The following analytical scheme for the analysis of selected plastics is divided into three parts. The first is devoted to the identification of plastics. The second contains procedures that are, with minor modifications, applicable to the analysis of most plastics. The third contains procedures for the analysis of specific plastics.

<sup>2</sup> Gehman, S. D., *Ind. and Eng. Chem.*, **44**, 730, 1952.

# **PART 1**

## **IDENTIFICATION OF PLASTICS**

Many schemes for the identification of plastics have been devised based on solubility, density, burning tests, and elemental analysis. The shortcomings of most of these schemes is their inability to characterize sufficiently the composition of copolymers or polymer blends.

The following scheme is based on an infrared spectrometric examination of the plastic film and a gas chromatographic examination of the plastics pyrolysis products.

### **IDENTIFICATION BY INFRARED SPECTROMETRY<sup>3 4 5 6</sup>**

Many commercial plastics contain plasticizers or other additives that may contribute some infrared absorption characteristic of functional groups other than those of the polymer. Elimination of these interfering materials may be accomplished according to the procedure in Part 2 for the determination of organic additives p 2045.

The absorption bands characteristic of the individual homopolymers are discussed below. The infrared spectrum of a copolymer is essentially a superposition of the component homopolymer spectra. Thus, the infrared spectrum can easily enable the identification of the components of a copolymer or a blend of polymers. To determine whether the plastic is actually a copolymer or a blend of polymers the plastic must be fractionated as prescribed in the procedure for fractional precipitation p 2047, and the fractions reexamined.

**Procedure**—Add 2 to 2.5 g of the plastic material to 50 ml of methylene chloride or other suitable low boiling solvent contained in a 4 oz bottle. Stopper the bottle and shake the solvent/plastic mixture until the plastic is dissolved or dispersed into small gel particles. Spread a portion of the resultant solution uniformly over the surface of a rock salt plate. Dry the solution on the plate slowly at room temperature and pressure to avoid the formation of bubbles in the film. After most of the solvent has been volatilized at room temperature, place the plate under a heat lamp for 10 to 20 min to remove all traces of the solvent. The resultant film should be approximately 0.1 mm thick. The desired thickness may be obtained by building up layers progressively. Obtain the infrared spectrum of the film from 2.5 to 15  $\mu$ .

<sup>3</sup> U. S. Dept. of Commerce, Office of Technical Services PB111438, 1954.

<sup>4</sup> Robert, A., Association Tech. de Lind, Tapatecture, Bulletin (6), 195, 1958.

<sup>5</sup> Potts, W. J., International Symposium on Plastics Testing and Standardization, ASTM, Philadelphia, 1958.

<sup>6</sup> The infrared spectra are reproduced from Nyquist, R. A., Infrared Spectra of Plastics and Resins, The Dow Chemical Co., Midland, Michigan, 1960.

**Polystyrene.**—The primary identifying infrared absorption bands for polystyrene are those at 13.2 and 14.3  $\mu$ , which arise from the monosubstituted benzene ring, and at 3.4 and 3.5  $\mu$ , which arise from the aliphatic methylene structure (Fig. 41-1).

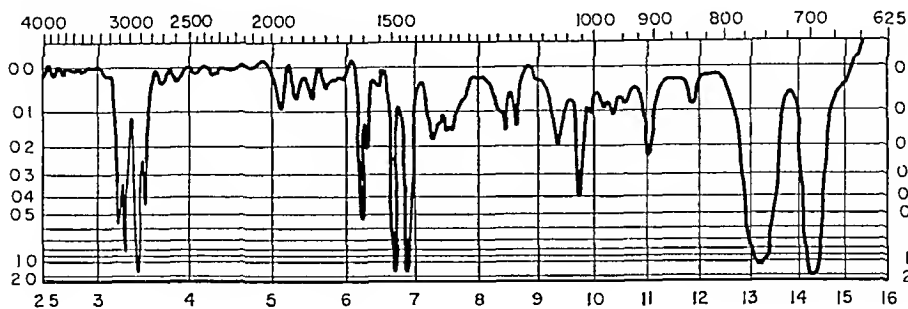


FIG. 41-1. Polystyrene.

**Polyacrylonitrile.**—Polyacrylonitrile is characterized by a sharp band at 4.5  $\mu$ , due to the  $\text{—C}\equiv\text{N}$  stretching vibration (Fig. 41-2).

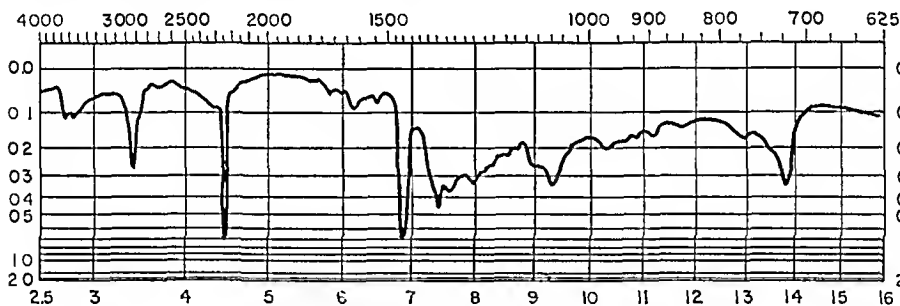


FIG. 41-2. Polyacrylonitrile.

**Butadiene Rubber.**—Most butadiene/styrene rubber used in styrene/rubber plastics contains butadiene, which has been polymerized primarily by trans 1,4- addition. A sharp band at 10.35  $\mu$  is characteristic of the trans- $\text{RCH=CHR}_1$  configuration (Fig. 41-3).

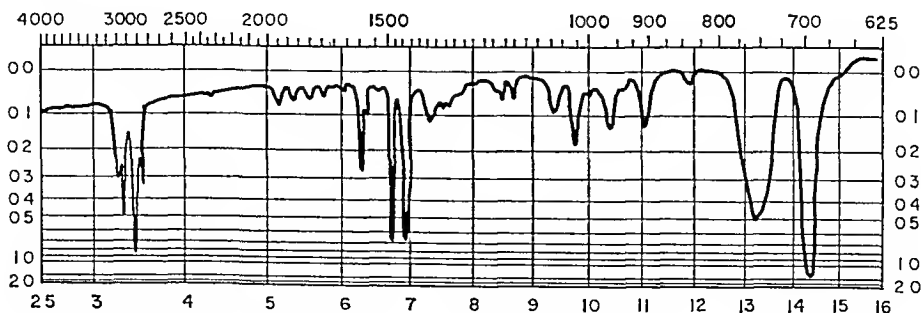


FIG. 41-3. Polystyrene-Rubber Blend.



**Polyvinyl Chloride**—The principal identifying absorption bands for polyvinyl chloride are those at  $7.0\ \mu$  due to C—H stretching and bending in the methylene groups at approximately  $9.2\ \mu$  and a broad band at  $14.5\ \mu$  which probably involves a C—Cl stretch (Fig 41.4)

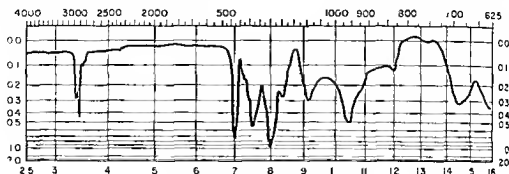


FIG 41.4 Polyvinyl Chloride

**Polyvinyl Acetate**—Polyvinyl acetate is characterized by sharp absorption bands at  $5.74\ \mu$ ,  $7.0\ \mu$  and  $7.26\ \mu$  and the absence of bands at  $9.2\ \mu$  and  $14.5\ \mu$ . The band at  $5.74\ \mu$  is due to the C=O group while the  $7.26\ \mu$  band arises from the methyl group (Fig 41.5)

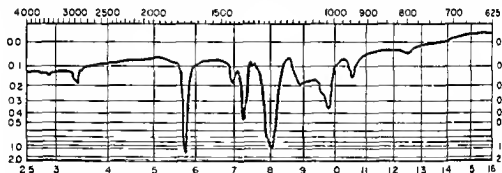


FIG 41.5 Polyvinyl Acetate

**Polyvinyl Alcohol**—The primary identifying bands for polyvinyl alcohol occur at  $3.03\ \mu$  and  $9.2\ \mu$ . These bands are caused by the —OH stretching and bending modes respectively (Fig 41.6). Bands characteristic of polyvinyl acetate normally occur in the spectra of polyvinyl alcohol since polyvinyl alcohol is made from polyvinyl acetate.

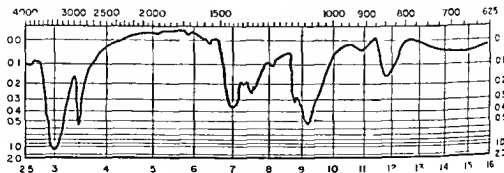


FIG 41.6 Polyvinyl Alcohol

**Polyvinylidene Chloride.**—Polyvinylidene chloride is characterized by an absorption band at  $7.1\ \mu$  and a doublet at about  $9.35$  and  $9.6\ \mu$  (Fig. 41-7).

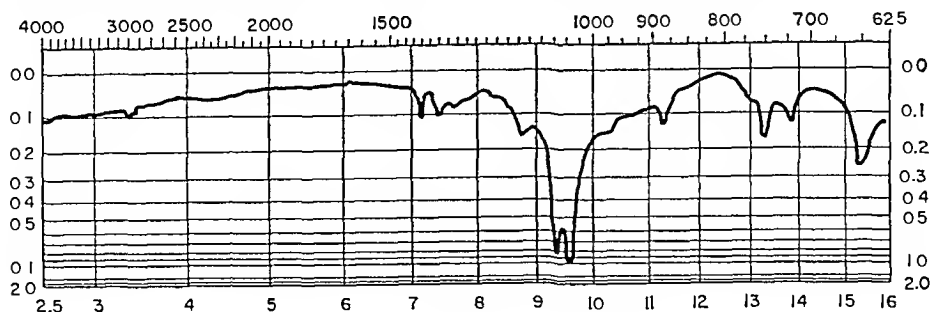


FIG. 41-7. Polyvinylidene Chloride.

**Vinyl Chloride/Vinylidene Chloride Copolymers.**—The vinyl chloride absorption band, which appears at  $8.0\ \mu$  in polyvinyl chloride, is shifted to  $8.3\ \mu$  in the random copolymers (Fig. 41-8).

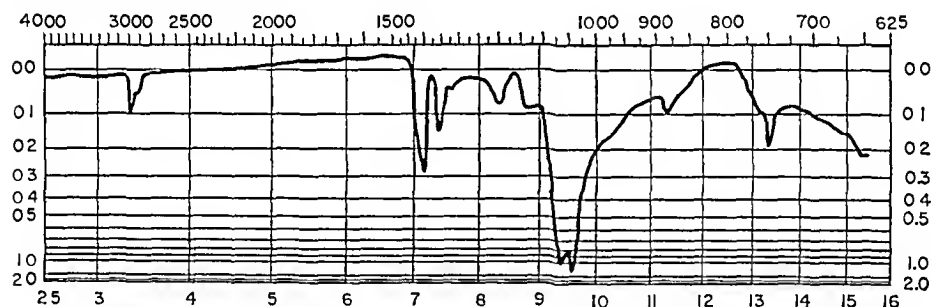


FIG. 41-8. Vinyl Chloride/Vinylidene Chloride Copolymer.

**Polyethylene.**—Polyethylene is identified by the carbon-hydrogen absorption bands, particularly the doublet between  $13.5$  and  $14.0\ \mu$ , which is found in all solid polyethylenes. The  $13.7\text{-}\mu$  band is sensitive to crystallinity. The melted polymers exhibit only the band at  $13.9\ \mu$ . The spectrum of branched polyethylene (low density) exhibits absorption at  $7.25\ \mu$ , due to the methyl groups, while linear polyethylene (high density) usually has a more intense band at  $11.0\ \mu$ , arising from the vinyl unsaturation (Fig. 41-9).

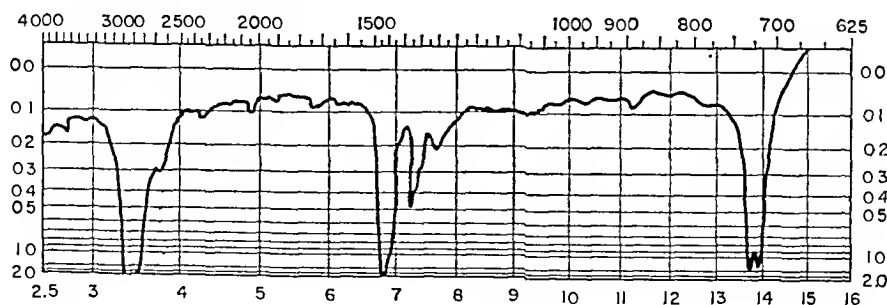


FIG. 41-9. Polyethylene.

**Acrylic Plastics**—The acrylic plastics are characterized by the presence of the typical  $C=O$  absorption at  $5.77 \mu$  absorption in the 8 to  $9 \mu$  region due to the  $C-O-C$  stretching mode and the absence of absorption bands at  $7.0$  and  $9.5 \mu$  (Figs 41 10 and 41 11). Characterization of the various alkyl esters of methacrylic and acrylic acids is accomplished by the pyrolysis gas chromatography procedure.

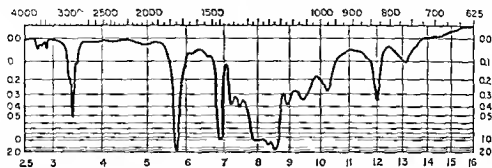


FIG 41 10 Polymethyl Acrylate

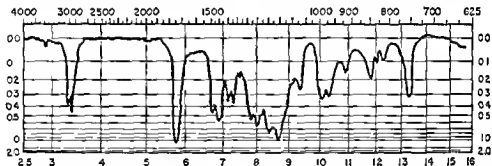


FIG 41 11 Polymethyl Methacrylate

**Cellulose Acetate** Cellulose acetate is identified by the presence of the weak hydroxyl absorption band at  $2.87 \mu$ , the strong carbonyl absorption at  $5.71 \mu$  and the broad absorption band at  $9.4 \mu$  together with the absence of the  $7.0\text{-}\mu$  band (Fig 41 12).

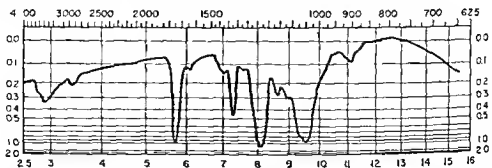


FIG 41 12 Cellulose Acetate

**Cellulose Ethers**—Cellulose ethers can be identified by the hydroxyl band at  $2.87 \mu$ , the broad cellulose ring absorption band between  $9.0$  and  $9.5 \mu$  and the

absence of absorption bands at 5.7 and 6.0  $\mu$ . Ethyl cellulose is characterized by absorption bands at 8.5 and at 10.4  $\mu$  (Fig. 41-13).

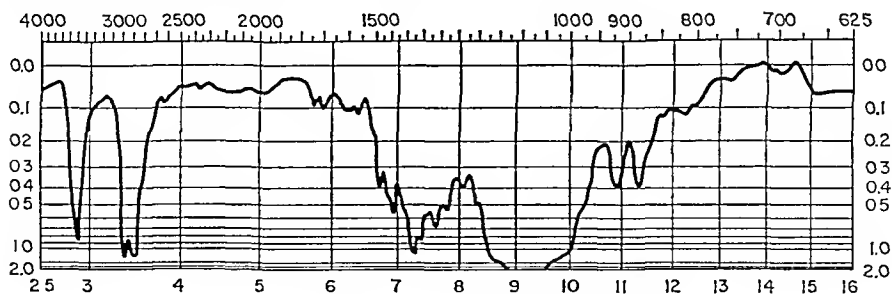


Fig. 41-13. Ethyl Cellulose.

### IDENTIFICATION BY PYROLYSIS-GAS CHROMATOGRAPHY<sup>7,8</sup>

**Scope.**—The pyrolysis-gas chromatographic procedure given below is designed primarily for the characterization of acrylic and methacrylic acid ester polymers and copolymers. The procedure is, however, applicable for the characterization of most polymeric materials.

When a polymer is heated above its ceiling temperature in an inert atmosphere, it will usually decompose to a specific number of components. Some polymers, such as polystyrene, the polyacrylates, and polymethacrylates, actually depolymerize, yielding large amounts of monomers. Others, such as polyvinyl chloride, polyvinyl acetate, and polyethylene, decompose, yielding a variety of low molecular weight products. The degradation products of copolymers are likely to be more complex than the products from the individual homopolymers or even blends of the homopolymers. Nevertheless, the depolymerization or decomposition products are characteristic of the individual plastic, provided all conditions are strictly controlled. Absolute identification of complex materials can be made by comparing the chromatograms with those obtained from known plastics. Normally, however, sufficient information can be obtained if the chromatograms are examined for the main pyrolysis products of the various polymers.

**Apparatus.** Pyrolysis Cell.—Equipped with a helium gas by-pass arrangement for attachment to the gas chromatograph (Fig. 41-14).

Gas Chromatograph.<sup>9</sup>

**Column.**—An 8-ft. length of 3/4-in. stainless steel tubing, packed with 20% di-2-ethylhexyl sebacate on firebrick (42 to 60 mesh).

**Thermal Conductivity Cell.**—Gow-Mac Model TE-II, or equivalent.

**Recorder,** 0 to 5 mv.

**Operating Conditions.**—(a) Helium flow rate, 60 ml. per min.; (b) current, 200 ma.; (c) column temperature, 69°C.; (d) chart speed, 24 in. per hr.

**Procedure.**—Weigh 5 to 10 mg. of the purified sample into the micro porcelain boat, and insert the boat into the heating coils. Assemble the pyrolysis cell as shown in Fig. 41-14. Sweep the cell with helium until all of the air is removed.

<sup>7</sup> Miller, D. L., Samsel, E. P., and Cobler, J. G., paper presented at the Regional Meeting of the American Chemical Society, Detroit, 1960.

<sup>8</sup> Radell, R. S., and Strutz, H. C., *Anal. Chem.*, **31**, 1890, 1959.

<sup>9</sup> Golke, R. S., *Anal. Chem.*, **29**, 1723, 1957.

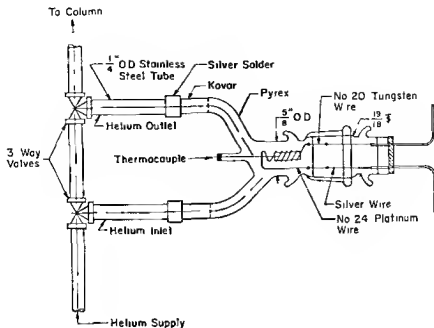


FIG. 41 14 Decomposition Chamber for Pyrolysis Gas Chromatographic Analysis

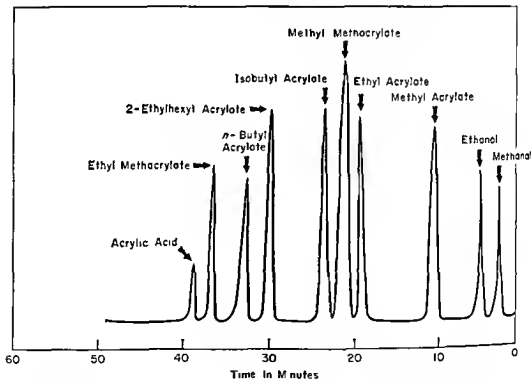


FIG. 41 15 Gas Chromatogram of Pyrolysis Products of Acrylate and Methacrylate Polymers

Close the by-pass valves, shutting off the flow of helium through the cell. Pyrolyze the sample at 500°C. for 60 sec. Open the by-pass valves, and allow the stream of helium to sweep the pyrolysis products into the column. After 30 sec., close the valves and develop the chromatogram in the usual manner. Record the thermal conductivity of the helium effluent as a function of time.

Calculations.—Compare the retention times of the various peaks with the retention times of the peaks formed by the pyrolysis of known polymers under the same conditions.

The retention times for the various methacrylic and acrylic acid esters from polymers pyrolyzed under the above conditions are shown in Fig. 41-15.

## PART 2

# GENERAL PROCEDURES

### PREPARATION OF SAMPLE

Most of the procedures require a ground or otherwise finely subdivided sample. Plastics may be reduced to the required size by comminution or by grinding in a mill such as a hammer mill, Wiley mill, or Multicut mill. Excessive heating in the mill may result in the loss of volatile constituents and adherence of the softened plastic to the internal parts of the mill. To prevent overheating, cool the mill thoroughly by passing dry ice through it prior to adding the sample. Mix 4 parts of crushed dry ice with 1 part of plastic. When both the mill and plastic are thoroughly chilled, grind the plastic to pass an ASTM No. 55 (500  $\mu$ ) sieve.

### DETERMINATION OF ADDITIVES AND PREPARATION OF ADDITIVE-FREE RESIN

**Scope**—The following procedures are suitable for determining the additive content of plastics and for preparing an additive-free or purified resin suitable for further characterization.

#### SURFACE ADDITIVES

Surface additives are normally lubricants used to prevent the polymer from sticking to the mold, antistatic agents and/or antidusting agents. The concentration of these agents may vary from 0.05% to about 1%. Surface additives are usually incompatible with the polymer, thus preventing their absorption into the body of the polymer. These agents may be mineral oil or waxes, ester waxes, fatty acids or their derivatives, aliphatic amides, and polyethers. Surface additives are isolated by extraction procedures using a polymer nonsolvent.

**Procedure**—Wash 400 g. of the unground plastic with three 500 ml. portions of a hot nonsolvent, such as methanol or ethanol. Cool the combined extracts to room temperature. Some surface additives have a low solubility in alcohol, and separate out on cooling. Filter off any insoluble material, dry, and weigh. Evaporate the filtrate to dryness on a steam bath. Dry the beaker and contents to constant weight at 70°C. The nature of the isolated surface additives may be determined by infrared spectrometry.

Dry the extracted plastic in a vacuum oven at 70°C for 2 hr., or until all the solvent has been removed. Retain the dried plastic for further characterization.

**Calculations**—

$$\text{Total surface additives, per cent} = \frac{\text{total weight of residues in grams}}{\text{sample weight in grams}} \times 100$$

## INORGANIC ADDITIVES

*Procedure.*—Weigh 4 g. of plastic reserved from the above procedure into a 100-ml., tared, conical centrifuge tube. Add 80 ml. of a suitable solvent (see "Reagents," below, p. 2046). Warm the tube and contents in a water bath, stirring occasionally until the plastic is in solution. Allow the solution to cool to room temperature. Centrifuge at 2600 r.p.m. for 30 min., or until the supernatant liquid is clear. Decant the solution into a 150-ml. beaker. Add 10 ml. of the solvent to the centrifuge tube, washing down the sides of the tube. Stir the residue with a stirring rod and repeat the centrifuging. Transfer the wash solution to the beaker. Repeat this washing with a second 10-ml. portion of the solvent. Dry the tube and contents on the water bath for 10 to 15 min. and then for 1 hr. at 105°C. (If a high boiling solvent is used, it may be necessary to dry the residue in a vacuum oven.) Cool the tube and contents in a desiccator, and reweigh.

The nature of the inorganic additives may be determined by suitable techniques such as emission spectrography or X-ray diffraction analysis.

Calculations.—

$$\text{Inorganic fillers, per cent} = \frac{\text{weight of residue}}{\text{weight of sample}} \times 100.$$

## ORGANIC ADDITIVES

Although the organic additive fraction will contain numerous products such as antioxidants, organic heat and light stabilizers, and low molecular weight polymers, the primary component will be the plasticizer. The plasticizer content of plastics may vary from 0.5% to several per cent. Plasticization is primarily a solvent action, the purpose being to aid in molding or compounding, or to otherwise modify the properties of the finished product. Plasticizers include such materials as esters, waxes, or low molecular weight polymers. Plasticization obtained by building the plasticizer into the polymer chain is termed internal plasticization. Internally plasticized polymers are actually copolymeric materials and, as such, will be treated under the appropriate sections.

*Procedure.*—Weigh 4 g. of the plastic, reserved from the second paragraph of the Procedure, above, into a 150-ml. beaker. Add 100 ml. of a suitable solvent. Warm the beaker and contents on a steam bath, and stir until dissolved. (If the inorganic additives were determined as directed above, the centrifugate may be used in place of preparing a separate solution.) Transfer the solution rapidly, while stirring, to an 800-ml. beaker containing 500 ml. of a polymer nonsolvent. (Suitable nonsolvents are given under "Reagents," below.) Rinse the 150-ml. beaker with 25 ml. of the nonsolvent, and transfer all of the contents to the 800-ml. beaker. Heat on the steam bath for 15 to 20 min., while stirring, until the precipitate is coagulated. Remove, and allow to cool to room temperature. Filter with suction through a weighed, medium-sintered glass crucible. Use two 50-ml. portions of the nonsolvent for transferring all the contents of the beaker to the crucible, and for washing the precipitate. Dry the crucible and contents to constant weight in a vacuum oven at 70°C. Combine the filtrate and washings, and evaporate almost to dryness on the steam bath. Transfer the container and contents to a vacuum desiccator and dry to constant weight (16 to 24 hr.).

If high boiling solvents were used, the drying may be performed in a vacuum oven at 70°C. Monomers and certain low molecular weight additives may be volatilized during this operation, however.



The additives may be characterized by suitable analytical procedures, such as infrared spectrometry and functional group analysis

Calculations.—

$$\text{Organic additives, per cent} = \frac{\text{weight of organic additive fraction}}{\text{weight of the original sample}} \times 100$$

## MOLECULAR WEIGHT DISTRIBUTION AND FRACTIONATION OF PLASTICS

*Scope*—The following methods are suitable for determining the molecular weight distribution or the weight fraction distribution of plastics. The molecular weights of the components of an individual plastic range from those of monomers and dimers to products that are 5 to 10 times the average molecular weight; thus, no one molecular weight value is fully satisfactory for the characterization of such a mixture.

The fractional precipitation procedure is also suitable for separating polymer blends and for characterizing block or graft polymers which normally have solubility characteristics intermediate between the pure homopolymeric forms.

The polymers are separated on the basis of their solubility in various solvents. In general, chemical and structural similarity between solvent and polymer favor solubility. Sometimes, however, mixed solvents exhibit greater solvent action than pure liquids. When mixed polar groups are present, each solvent may solvate one particular group. In the solvation process, one polar group may be strongly attracted to the polar group of the solvent, the nonpolar or less polar group being directed outward. The addition of a nonpolar solvent reduces the polarity of the medium nearer to that of the solvated molecule. It must be remembered, however, that solubility will also be affected by such things as branching, cross-linking, crystallinity, and variations in copolymer content. Normally, increasing the molecular weight, crystallinity, or melting point will decrease the solubility in a given solvent.

*Principle*—The plastic is dissolved in a suitable solvent and fractionally precipitated by the addition of a nonsolvent. High molecular weight polymers are precipitated first. The fractions obtained, however, are never homogeneous with respect to molecular weight. The efficiency is greater the more dilute the solution and it is greater in the lower molecular weight ranges.

*Reagents*.—

<i>Plastic</i>	<i>Solvent</i>	<i>Nonsolvent</i>
polystyrene	benzene or methyl ethyl ketone	methanol
polyethylene (4000–40,000)	toluene at 80°C	n-propyl alcohol
polyvinyl chloride	tetrahydrofuran	water
polyvinyl chloride-acetate	hot o-dichlorobenzene	warm ethanol
polyacrylonitrile	N,N-dimethylformamide	1:1 heptane-ether
styrene-acrylonitrile copolymer	methyl ethyl ketone	methanol
polymethyl methacrylate	acetone	petroleum ether, b.p. 40 to 60°C

## CUMULATIVE WEIGHT DISTRIBUTION

*Procedure.*—Weigh 1 g. of plastic into each of ten 16-oz., wide-mouth, screw cap (foil lined) bottles. Add 100 ml. of solvent to each bottle, and stopper tightly. Shake the bottles occasionally until the polymer is dissolved.

Titrate the solutions with a nonsolvent, thereby precipitating the polymer, which is then isolated, dried, and weighed. Titrate the first sample, adding the titrant slowly with constant stirring, to the appearance of a turbidity. Titrate the remaining samples empirically with increasing amounts of the nonsolvent. The usual increments are of 1 ml. The final titration should precipitate all the polymer.

Increased homogeneity of precipitates may be obtained by warming the solutions to redissolve the precipitates, and then allowing the solutions to cool slowly. Stopper the bottles and allow them to stand 24 hr. to assure establishment of equilibrium between the 2 phases. Filter the solutions through tared, coarse porosity, fritted glass filters. Where the formation of a filterable precipitate does not occur, the supernatant phase may be removed by centrifuging and decanting. Allow the solvent to drain completely, and then wash the precipitates with ethanol. Dry under vacuum at 80°C. for 4 hr. and weigh.

*Calculations.*—Prepare a weight distribution curve by plotting the weight fraction of polymer precipitated on the ordinate axis against the number of milliliters of precipitant on the abscissa.

The molecular weight of the fractions may be determined and plotted similarly.

A cumulative weight distribution curve, which gives the amount of material with a molecular weight less than  $M$ , can be prepared by plotting the calculated weights of material left in solution versus the molecular weights ( $M$ ) of the precipitated fractions.

## FRACTIONAL PRECIPITATION

*Procedure.*—Dissolve 5 g. of polymer in 500 ml. of a suitable solvent. Titrate the entire solution with a nonsolvent to the appearance of a precipitate. Warm the solution to dissolve the precipitate, and then let it cool slowly to reprecipitate the polymer. Allow the solution to stand 24 hr. to attain equilibrium. Decant or filter the supernatant solution. Titrate the isolated solution and remove the precipitate as described above. Continue this cycle until all of the polymer has been precipitated. Dry all residues under vacuum at 80°C. for 4 hr.

*Calculations.*—Prepare a weight distribution curve as described under "Calculations," above.

DEFINITIONS OF MOLECULAR WEIGHT<sup>10</sup>

Molecular weight measurements may be classified as two main types: equilibrium measurements, involving osmotic pressure and ultracentrifuge methods; and kinetic measurements, involving viscosity and light-scattering techniques. Since most polymers contain a rather wide distribution of molecular weights, the molecular weight value obtained on an unfractionated polymer will be an average molecular weight. Owing to the different properties measured, different types of averages are obtained. The most common averages are the number average ( $\bar{M}_n$ ), the weight average ( $\bar{M}_w$ ), the viscosity average ( $\bar{M}_v$ ), and the z-average ( $\bar{M}_z$ ).

Homogeneous polymers containing only one size molecule give  $\bar{M}_w$  and  $\bar{M}_n$  values

<sup>10</sup> Schmidt, A. X., and Marlies, C. A., *Principles of High Polymer Theory and Practice*, McGraw-Hill, New York, 1948. Reproduced with permission.

that are equal. When a size distribution of molecules exists,  $\bar{M}_w$  will be greater than  $\bar{M}_n$ , and the difference will increase as the size disparities increase. For example, equal parts by weight of molecules with molecular weights of 10,000 and 100,000 will give a  $\bar{M}_n$  of 18,200 and a  $\bar{M}_w$  of 55,000. Equal numbers of molecules with molecular weights of 10,000 and 100,000, however, will give a  $\bar{M}_n$  of 55,000 and a  $\bar{M}_w$  of 92,000.

$\bar{M}_n$  is obtained by dynamic or equilibrium osmotic pressure measurements, where each molecule affects the measured property regardless of shape, size, or flexibility. Thus,  $\bar{M}_n$  is the average molecular weight in the classical sense

$$\bar{M}_n = \frac{\text{total mass}}{\text{total number of moles}}$$

$\bar{M}_v$  is obtained by viscosity measurements that are influenced not only by the number of molecules present, but also by their shape and size. The accuracy of viscosity molecular weights is  $\pm 10\%$  in the range 25,000 and higher. The equations for calculating the molecular weights, however, contain empirical constants that must be obtained by measurements on polymers of known molecular weights determined by some other method.

Light scattering techniques may be used for making molecular weight measurements from 10,000 up; indeed, the precision of the measurement increases with increasing molecular weight. In making measurements, a beam of monochromatic light of known intensity is passed into a dilute polymer solution. The molecular weight ( $\bar{M}_w$ ) is calculated from the intensity of the light scattered at right angles and from the refractive indices of the solvent and of the solution. The angular distribution (dissymmetry) between  $30^\circ$  and  $150^\circ$  of the intensity of the scattered light, furnishes information concerning the size and shape of the molecule. This information can be augmented by studying the depolarization of the scattered light.

A wide range of molecular weights can be determined in the ultracentrifuge by 2 sedimentation methods: velocity and equilibrium. Measurements by the velocity method require centrifugal forces of 10,000 to 1,000,000 times gravity, but may be completed in several hours. This procedure measures the rate of fall of the boundary separating the solution from the pure solvent. The equilibrium method requires less centrifugal force (1,000 to 100,000 times gravity) but may take several days to complete. One determines by this procedure the distribution of particles when the rate of diffusion (the tendency of a molecule to move from a region of high concentration to a region of low concentration) and the rate of sedimentation are equal. Weight average molecular weights are generally obtained by the sedimentation velocity technique. Molecular weights by the sedimentation-equilibrium technique may be either weight average ( $\bar{M}_w$ ) or z-average ( $\bar{M}_z$ ) values. If the concentration of the polymer is determined by light absorption measurements,  $\bar{M}_w$  is obtained.  $\bar{M}_z$  is obtained by measuring the concentration by refractive index techniques.

## METALLIC IMPURITIES <sup>11</sup>

**Scope.**—This method provides for the rapid quantitative determination of eleven or more metallic elements at the trace level.

**Standards.**—(a) Prepare a spectroscopic buffer solution by dissolving 20 g of Mallinckrodt A R Grade  $\text{NaNO}_3$ , and 75 ml of distilled  $\text{HNO}_3$  in water. Add

<sup>11</sup> Bartel, J. F., The Dow Chemical Co., unpublished manuscript.

1.6 ml. of 0.01% Mo, and 0.8 ml. of 1.0% Bi, and dilute to 100 ml. with water. The Mo and Bi are added to provide internal reference lines. (b) Prepare a 0.01% impurity solution containing Al, Ca, Cu, Fe, Mg, Mn, Ni, Pb, Sn, Sr, and Zn. Each element must be present at a concentration of 0.1 mg. per milliliter. Dilute 2.5 ml. of this solution to 25 ml., to give a 0.001% impurity solution (0.01 mg. per milliliter). (c) Prepare the following set of standards by pipetting the specified amount of impurity solution into a test tube, adding a few drops of  $\text{H}_2\text{SO}_4$ , to convert to the sulfate, and evaporating to dryness. Add 1 ml. of  $\text{HNO}_3$  to the test tube, and evaporate to dryness.

*Blank*

0.00005%—0.25 ml. of the 0.001% impurity solution  
0.0001%—0.5 ml. of the 0.001% impurity solution  
0.0005%—2.5 ml. of the 0.001% impurity solution  
0.001%—0.5 ml. of the 0.01% impurity solution  
0.0025%—1.25 ml. of the 0.01% impurity solution  
0.005%—2.5 ml. of the 0.01% impurity solution  
0.01%—5.0 ml. of the 0.01% impurity solution

(d) To the residue in the test tubes, add 5.0 ml. of the buffer solution, and warm until dissolved. The impurity solutions can be varied to provide different sets of standards until all desired elements are covered.

**Loading.**—Polish the ends of  $\frac{1}{4}$ -in. diameter and  $\frac{1}{2}$ -in. length graphite electrodes on filter paper, and place in every other row in a stainless steel tray. Samples are run in duplicate thus requiring 4 electrodes. Add a drop of kerosene to the tops of the electrodes to seal the porosity, and allow to dry. Pipet 0.03 ml. of the standard solution onto the ends of the electrodes, and dry over micro burners in a gas drying oven, leaving a salt cap deposit. Store the electrodes in a desiccator until run.

**Operating Conditions.**—(a) Baird 3-meter grating spectrograph; (b) 2150 A—3550 Å region; (c) SA No. 2 plate; (d) 50- $\mu$  slit; (e) 32-cm. lens; (f) 4.8-amp., a.c. arc source; (g) 10-sec. pre-exposure; (h) 90-sec. exposure; and (i) 2-mm. gap.

**Plate Calibration.**—Photograph a d.c. arc spectrum of an iron bead through a 3-step filter of 15, 50, and 85% transmission. Determine the densities of several lines at the 50 and 85% levels by means of a nonrecording densitometer. Plot these values on linear graph paper to provide a preliminary response curve. Points from this curve are plotted for the final response curve, using the log ratio for the wavelength being used.

**Photographic Plate Processing.**—Develop the plate at 20.5°C. for  $3\frac{1}{2}$  min., with continuous agitation, in a Kodak D-19 developer. Insert the plate into a chrome alum hardener for 1 min., and fix in X-ray fixer for 2 min. After washing in running water for 3 min., sponge the plate to remove excess water, and dry over an air-blown heater.

**Analytical Curves.**—Obtain the densities of selected lines of the impurity elements and the internal reference elements Mo and Bi, by the use of the densitometer. Calculate the log density ratios from the plate response curve. Plot these values against concentration on logarithmic graph paper. The following list shows the line pairs used and the useful percentage range.

<i>Element</i>	<i>Line</i>	<i>Reference Line</i>	<i>Percentage Range</i>
Al	3092 71	3132 59 Mo	0 00005-0 001
Al	3082 16	3132 59 Mo	0 00005-0 001
Al	2660 39	3132 59 Mo	0 001-0 01
Ca	3179 33	2897 98 Bi	0 0005-0 01
Cu	3273 96	3132 59 Mo	0 0001-0 0025
Cu	3247 54	3132 59 Mo	0 00005-0 001
Fe	3021 07	3132 59 Mo	0 0001-0 01
Fe	3020 64	3132 59 Mo	0 00005 0 005
Fe	2483 27	3132 59 Mo	0 0005-0 01
Mg	2802 69	3132 59 Mo	0 00005-0 0005
Mg	2795 53	3132 59 Mo	0 00005-0 0005
Mg	2779 83	3132 59 Mo	0 0005-0 01
Mn	2933 06	3132 59 Mo	0 0005 0 01
Mn	2801 06	3132 59 Mo	0 00005-0 001
Ni	3414 77	3132 59 Mo	0 00005-0 001
Ni	3134 11	3132 59 Mo	0 0005 0 01
Pb	2873 32	2897 98 Bi	0 0005-0 01
Pb	2833 07	2897 98 Bi	0 00005-0 005
Sn	3175 02	3132 59 Mo	0 00005 0 005
Sn	3034 12	3132 59 Mo	0 0001-0 01
Sr	4077 71	3902 96 Mo	0 00005-0 0005
Sr	3464 57	3132 59 Mo	0 0005-0 01
Zn	3345 02	2897 98 Bi	0 001-0 01
Zn	3345 02	Background	0 0001 0 01

**Procedure**—Weigh 0.4 g of sample directly into a 10 ml kjeldahl flask. Char the sample to dryness in the presence of  $\text{H}_2\text{SO}_4$ . Add 1 ml of  $\text{H}_2\text{SO}_4$ . Add  $\text{HNO}_3$  dropwise to the solution and continue heating until the oxidation is nearly completed. Add a few drops of  $\text{HClO}_4$  to finish the process. Evaporate the solution to dryness over a Meker burner and allow the flask to cool. Add a small amount of  $\text{HNO}_3$  and again evaporate to dryness. Carry a blank of the distilled acids through the same procedure as a control. Take the sample up in 0.4 ml of the spectroscopic buffer solution and load as directed under Loading above. The percentage range of the analytical curves can be extended by concentration or dilution of the sample solution.

**Calculations**—Obtain the densities of selected lines of the impurity elements and the internal reference elements Mo and Bi. Calculate the log density ratios from the plate response curve. Read from the analytical curve the percentage of metallic impurity corresponding to the log density ratio.

### SULFATED OR SULFONATED EMULSIFIERS IN EMULSION POLYMERIZED RESINS<sup>12</sup>

**Apparatus** Spectrophotometer—Suitable for measurements at 650 m $\mu$

**Reagents**—Dissolve 250 mg of methylene blue USP grade in 1 liter of distilled water

**Calibration Curve.**—Prepare a standard solution containing 1.0 mg. of the desired emulsifier per 100 ml. Transfer from 1 to 5 ml. of the standard solution to 250-ml. separatory funnels.

Dilute to 100 ml. with water made just acid with dilute HCl. Add 1 ml. of the methylene blue solution to each funnel. Mix the contents, and add 20 ml. of  $\text{CHCl}_3$ . Shake vigorously for 1 min. Transfer the  $\text{CHCl}_3$  to a 125-ml. separatory funnel. Repeat the extraction with a second 20-ml. portion of  $\text{CHCl}_3$ . The remaining aqueous layer should contain excess methylene blue. Extract the combined  $\text{CHCl}_3$  extracts with 50 ml. of  $\text{H}_2\text{O}$  containing 3 drops of  $\text{H}_2\text{SO}_4$ . Filter the  $\text{CHCl}_3$  layer through a small plug of cotton into a 50-ml. volumetric flask. Wash the cotton plug with  $\text{CHCl}_3$ , catching the washings in the volumetric flask. Dilute to volume with  $\text{CHCl}_3$ . Transfer a portion of the solution to a 1-cm. absorption cell. Measure the absorbance of the solution at 650  $m\mu$ , using distilled water as the reference solution. Subtract the absorbance of a reagent blank from that of the samples.

Plot the number of milligrams of emulsifier against the absorbance readings.

**Procedure.**—Weigh approximately 2 g. of the finely subdivided plastic accurately into a small Soxhlet extraction thimble. Extract in a Soxhlet extractor with Formula 30 ethanol for 8 hr. Transfer the extract to a beaker, and evaporate to dryness on a steam bath. Dissolve the residue in water, warming if necessary, and transfer to a 100-ml. volumetric flask. Dilute to volume with water. Transfer a 5-ml. aliquot of the solution to a 250-ml. separatory funnel, and proceed as directed in the second paragraph of "Calibration Curve," immediately above.

**Calculations.**—Read from the calibration curve, the number of milligrams of emulsifier corresponding to the absorbance of the solution.

$$\text{Emulsifier, per cent} = \frac{\text{milligrams of emulsifier} \times 100}{\text{milligrams of sample in aliquot}}$$

## POLYETHER-TYPE EMULSIFIERS IN EMULSION POLYMERIZED RESINS<sup>13</sup>

**Apparatus.**—Spectrophotometer suitable for measurements at 430  $m\mu$ .

**Solvent Mixture.**—Mix 1 volume of ethylene glycol monomethyl ether with 1 volume of 2 *N* HCl.

**Calibration.**—Prepare a standard solution containing 0.5 mg. of the desired emulsifier per milliliter. Transfer 1- to 5-ml. aliquots of the solution to 50-ml. conical centrifuge tubes. Dilute to a total volume of 10 ml. with  $\text{H}_2\text{O}$ .

Add 1 ml. of 2 *N* HCl, followed by 2 ml. of 10%  $\text{BaCl}_2$  solution and 2 ml. of 10% phosphomolybdic acid solution. Mix the solutions and allow to stand for 1 hr. Centrifuge at 2500 r.p.m. for 10 min. Decant and discard the supernatant solution, taking care not to disturb the precipitate. Wash the precipitate with 3 ml. of 0.1 *N* HCl. Centrifuge as before, and decant, discarding the supernatant solution. Wash the sides of the centrifuge tube with a cotton swab wetted with water. Pipet exactly 25 ml. of the glycol-HCl solution into each tube. Warm the tube slightly on a steam bath to dissolve the precipitate. Cool to room temperature. Filter the solution through Whatman No. 42 filter paper, and transfer a portion of the filtrate to a 1-cm. absorption cell. Measure the absorbance of each solution at

<sup>13</sup> Shaffer, C. B., and Critchfield, F. H., *Anal. Chem.*, 19, 32, 1947.

430  $\mu$  using distilled water as a reference solution. Measure the absorbance of a reagent blank under the same conditions and subtract the absorbance from that of the samples.

Plot the number of milligrams of emulsifier versus the corresponding absorbance readings.

**Procedure**—Extract 2 g of sample as directed under Procedure of the preceding method. Transfer the ethanol extract to a beaker and evaporate to dryness on a steam bath. Dissolve the residue in 2 to 3 ml of water and transfer to a 50 ml centrifuge tube. Rinse the beaker with water and transfer to the tube. Use sufficient water to make a total volume of 10 ml. Proceed as directed in the second paragraph of Calibration above.

**Calculation**—Read from the calibration curve the number of milligrams of emulsifier corresponding to the absorbance reading.

$$\text{Emulsifier per cent} = \frac{\text{milligrams of emulsifier} \times 100}{\text{milligrams of sample}}$$

## INDEX OF REFRACTION OF TRANSPARENT PLASTICS<sup>14</sup>

**Scope**—The following methods are intended for the measurement of the index of refraction of transparent plastics. Two procedures, refractometric and microscopic, are covered. The refractometric method is more accurate and is to be preferred wherever it is applicable.

### REFRACTOMETRIC METHOD

**Apparatus** Refractometer—Abbe refractometer or equivalent.

Constant Temperature Bath—Adjusted to  $23^{\circ} \pm 1^{\circ}\text{C}$ .

Contacting Liquids

<i>Plastic</i>	<i>Contacting Liquid</i>
cellulose acetate	alpha bromonaphthalene
acrylic resins	saturated aqueous solution of zinc chloride made slightly acid
vinyl resins	alpha bromonaphthalene
styrene resins	saturated aqueous solution of potassium mercuric iodide

**Test Specimen**—Prepare a test specimen measuring about 0.25 in. by 0.5 in. on one face and having 1 end perpendicular to the face. Polish the face and end of the specimen on fine emery paper backed by a piece of plate glass followed by a polishing rouge suspended in water on a piece of parchment. The face of the specimen must be flat to provide good contact of the specimen and prism surfaces and must intersect the end without a beveled or rounded edge.

**Procedure**—Adjust the constant temperature bath to  $23^{\circ} \pm 1^{\circ}\text{C}$  and allow the refractometer to reach equilibrium. Clean the refracting prism surface with alcohol applied with lens paper. The hinged illuminating prism is not used and can be rotated away from the refracting prism. Place a source of diffuse white light so that good illumination is obtained along the plane of the surface of contact between the specimen and the refracting prism.

<sup>14</sup> ASTM Standards Pt. 9 D542.50 ASTM Philadelphia 435 1958

Place a drop of a suitable contacting liquid on the polished face of the specimen, and then place the specimen in firm contact with the surface of the refracting prism, with the polished end of the specimen toward the source of light.

Move the index arm of the refractometer until the field seen through the eyepiece is one-half dark. Rotate the compensator dial to remove all color from the field. Adjust the index arm by means of the vernier until the dividing line between the light and dark portions of the field exactly coincides with the intersection of the cross hairs. The manipulations should be performed rapidly to avoid changes in the refractive index of the plastic due to absorption of the contacting liquid.

**Calculations.**—Read the value of the index of refraction for the sodium *D* line directly from the instrument.

Determine the dispersion by reading the compensator dial and applying this figure, along with the index of refraction, to a chart or table supplied with the instrument.

**NOTE.**—In the case of nonisotropic materials, such as injection and compression molded materials, the index of refraction will be the average value for a thin layer of small area at a point of contact near the center of the refractometer prism. For a complete and accurate determination of the variation of the index through the test specimen, it is necessary to make the measurements at more than one point on the surface, and within the body of the material. This can be done by preparing a contacting surface both perpendicular and parallel to the molding pressure or flow. After the specimen is contacted to the prism it may be moved carefully along the prism surface in the direction of the light source while the variation of index is being followed.

### MICROSCOPIC METHOD

**Apparatus.**—Microscope, having a magnifying power of at least 200 diameters, and equipped with a means of measuring the longitudinal travel of the lens tube to within 0.001 in.

**Procedure.**—Prepare a specimen about 0.25 in. in thickness with 2 parallel surfaces. Place the specimen on the measuring microscope platform with the surface having the best polish nearest the objective. Focus the microscope through the specimen and on the bottom surface. Record the reading of the longitudinal displacement of the lens tube to the nearest 0.001 in. Without moving the specimen, focus the microscope on the top surface of the specimen, and again record the reading of the displacement.

**Calculation.**—The distance between the bottom and the top surfaces of the specimen is the apparent thickness. The index of refraction is found by dividing the actual thickness of the specimen by the apparent thickness.

### SPECIFIC GRAVITY OF PLASTICS <sup>15</sup>

**Scope.**—The following methods are intended for the determination of the specific gravity of plastics. The first method is suitable for use where the plastic is in a finished condition, such as sheets, rods, and molded articles. The second method is suitable for use with unfabricated plastics such as powder, pellets, and flake.

#### SPECIFIC GRAVITY OF PLASTICS IN FINISHED CONDITION

**Apparatus.** Analytical Balance.—The balance is equipped with a pan straddle or other stationary support.

<sup>15</sup> ASTM Standards, Pt. 9, D792-50, ASTM, Philadelphia, 526, 1958.



**Test Specimen**—Prepare a specimen weighing from 1 to 5 g. Smooth or trim the sides to free them from surface roughness that might entangle air bubbles when immersed in liquid.

Test specimens whose change in specific gravity on conditioning may be greater than the accuracy of the specific gravity method should be conditioned before testing.<sup>16</sup>

**Procedure**—Tare the balance with a piece of wire sufficiently long to reach from the hook on the pan support almost to the pan straddle. Attach the specimen to the wire so as to be suspended about 1 in. above the pan straddle and weigh. Record the weight as *A*. Place a beaker containing freshly boiled distilled water at a temperature of  $23^{\circ} \pm 2^{\circ}\text{C}$  on the pan straddle. Completely immerse the specimen in the water. Neither the plastic nor the supporting wire should touch any part of the beaker. Remove any adhering air bubbles with a fine wire. Weigh the suspended specimen and record the weight as *B*. Remove the specimen and replace the wire in the water to the same depth it was previously. Record the loss in weight of the wire on immersion as *C*. *C* may be neglected if *A*  $\geq$  10 g. No. 36 or finer wire is used.

**Calculation**—

$$\text{Sp. gr., } 23/23^{\circ}\text{C} = \frac{A}{A - B - C}$$

## SPECIFIC GRAVITY OF UNFABRICATED PLASTICS

**Apparatus** Analytical Balance

Pycnometer with Thermometer

Vacuum Desiccator—With suitable shield

Oil Vacuum Pump—Designed to give a vacuum of 3 mm. or less

Constant Temperature Bath—Adjust bath to  $23^{\circ} \pm 0.1^{\circ}\text{C}$

**Procedure**—Fill the pycnometer with freshly boiled distilled water and bring to a temperature of  $23^{\circ} \pm 0.1^{\circ}\text{C}$ . Remove any air bubbles by placing it in a vacuum desiccator and applying vacuum. Bring the system to equilibrium in the bath at  $23^{\circ} \pm 0.1^{\circ}\text{C}$ , then remove the pycnometer from the bath and fill it exactly to the tip. Dry the outside of the pycnometer and weigh it to the nearest 0.1 mg. Remove the water from the pycnometer, clean dry and reweigh. Add approximately 1 to 5 g. of the specimen to the pycnometer and reweigh. Add sufficient boiled distilled water to cover the specimen and repeat the above treatment.

**Calculations**—

$$\text{Sp. gr., } 23/23^{\circ}\text{C} = \frac{A}{B - C + A}$$

where *A* = weight in grams of specimen in pycnometer,

*B* = weight in grams of pycnometer filled with water, and

*C* = weight in grams of pycnometer containing the specimen and filled with water.

**NOTE**—Kerosene or other suitable liquid may be used for a plastic that is soluble in or otherwise affected by water. Methanol may be used if the plastic has a specific gravity below 1.0. When nonaqueous liquids are used as the immersing fluid, the specific gravity of the liquid at  $23^{\circ}\text{C}$  must be determined. The calculations given previously are corrected in this case by multiplying by the specific gravity of the liquid at  $23/23^{\circ}\text{C}$ .

<sup>16</sup> Pre testing conditioning should be done in accordance with directions given in Standard Methods of Conditioning Plastics and Electrical Insulating Materials, ASTM Standard Pt. 9 D618-58, ASTM Philadelphia 591 1958.

# PART 3

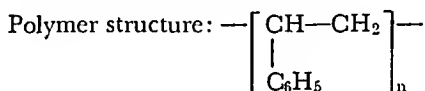
## PROCEDURES FOR THE ANALYSIS OF VARIOUS TYPES OF PLASTICS

### STYRENE PLASTICS

Styrene plastics are based on resins made by the polymerization of styrene or the copolymerization of styrene with other unsaturated compounds. The more common styrene copolymers are those containing acrylonitrile or methyl methacrylate.

### POLYSTYRENE

Monomer: styrene,  $\text{C}_6\text{H}_5\text{CH}=\text{CH}_2$



### METHANOL-SOLUBLE MATERIAL <sup>17</sup>

*Sample Preparation.*—Grind the sample to pass an ASTM No. 12 (1680- $\mu$ ) sieve.

*Apparatus.* Drying Oven.—The oven should be adjustable from 65° to 70°C.

Fine Porosity Sintered Glass Crucibles.

*Solvents.* Methanol, CP.—Redistilled.

Dioxane.—Store over NaOH, and redistill prior to use.

NOTE.—Because of space limitations, common laboratory equipment, chemicals, and standard solutions are not included in the lists of apparatus and reagents.

*Procedure.*—Wash all glassware with toluene, follow with an acetone rinse, and dry thoroughly. Dry the crucibles for 1 hr. at 65°C., and store in the desiccator. Weigh about 0.3 g. of the ground sample into a tared 50-ml. beaker (or weighing bottle), weighing to the nearest 0.0001 g. Add 15 ml. of dioxane, cover the vessel with a watch glass, and let stand until the sample is dissolved. After solution is complete, stir thoroughly, and transfer rapidly while stirring, to a 400-ml. beaker containing 200 to 250 ml. of redistilled methanol. Rinse the 50-ml. beaker with 25 to 50 ml. of methanol from a wash bottle, using a policeman if necessary to dislodge any solid particles. The transfer shall be quantitative.

Heat to 65°C. on the water bath or steam plate, while stirring, until the precipitate is fairly well coagulated, then remove and allow to settle for a few minutes. Filter with suction through a weighed, sintered glass crucible, first decanting as

<sup>17</sup> Standards on Plastics, ASTM, Philadelphia, 17, 1955.

much liquid as possible and then transferring the solids with the aid of a police man and methanol from a wash bottle

**NOTE**—The strictest quantitative technique shall be observed in handling the sample and the crucible

Use about 125 ml of methanol for transferring and washing the precipitate. Continue suction until dry. Clean the outside of the crucible with a damp cloth or chamois. Dry to constant weight at 60° to 70° C. Cool in a desiccator and weigh.

**Calculation**—

$$\text{Methanol soluble content per cent} = \frac{A - B}{A} \times 100$$

where  $A$  = weight of sample in grams and

$B$  = weight of precipitate in grams

### 10. VOLATILE MATERIAL <sup>15</sup>

**Apparatus** Weighing Dishes—Disposable aluminum dishes approximately 2 in. in diameter and 0.5 in. deep.

**Vacuum Oven** Abderhalden type employing 1,2,4 trichlorobenzene as the heat transfer liquid. See Fig. 41.16.

**Tray** Able to hold 4 weighing dishes. See Fig. 41.17.

**Procedure**—Weigh exactly 1 g. of plastic previously ground to pass a #40 screen (U. S. No. 12) into a dry tared weighing dish. Spread the sample evenly over the bottom of the dish. Place the dish in the tray. Four samples must be run at a time. If sufficient samples are not available the remaining spaces should be filled with dishes containing approximately 1 g. of polystyrene. Place the tray in the heated oven. Close the oven door and evacuate to 5 to 1 mm. Hg pressure. After exactly 25 min. withdraw the weighing dishes and place in a desiccator. When the samples are cool (20 min. or more) weigh the dish and sample.

**Calculations**—

$$\text{Volatile material per cent} = \frac{\text{loss in weight}}{\text{sample weight}} \times 100$$

### 11. STYRENE MONOMER ULTRAVIOLET SPECTROPHOTOMETRIC PROCEDURE <sup>16</sup>

**Scope**—This procedure is suitable for the determination of styrene monomer in polystyrenes that form clear solutions and do not contain dyes or other additives that absorb strongly in the ultraviolet region.

**Apparatus** Ultraviolet Spectrophotometer—Beckman DU or equivalent.

**Standardization**—Styrene monomer exhibits an absorption maximum and a minimum in the ultraviolet region at approximately 292.5 mμ and at 289.5 mμ respectively. The wavelengths must be determined for each spectrophotometer. Prepare a styrene standard solution containing 10 mg. of styrene monomer per 100 ml. of chloroform. Transfer a portion of this solution to a 1 cm. absorption cell. Measure the absorbance of the solution at 0.5 mμ intervals from 295 mμ to 285 mμ using chloroform as the reference solution.

<sup>15</sup> Haynes W. S. The Dow Chemical Co. unpublished data.

<sup>16</sup> Perry H. L. Anal. Chem. 23, 1337 (1951); Lovstrom E. I., Warren J. S. and Cobler J. G. The Dow Chemical Co. unpublished manuscript.

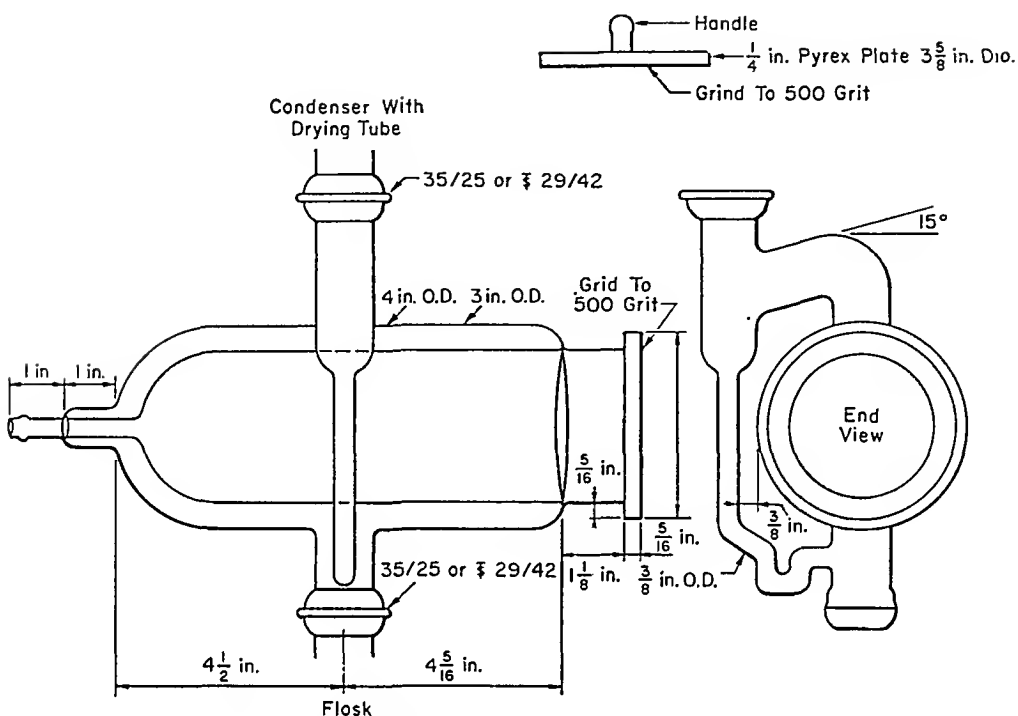


FIG. 41-16. Abderhalden Oven. (All Dimensions in Inches.)

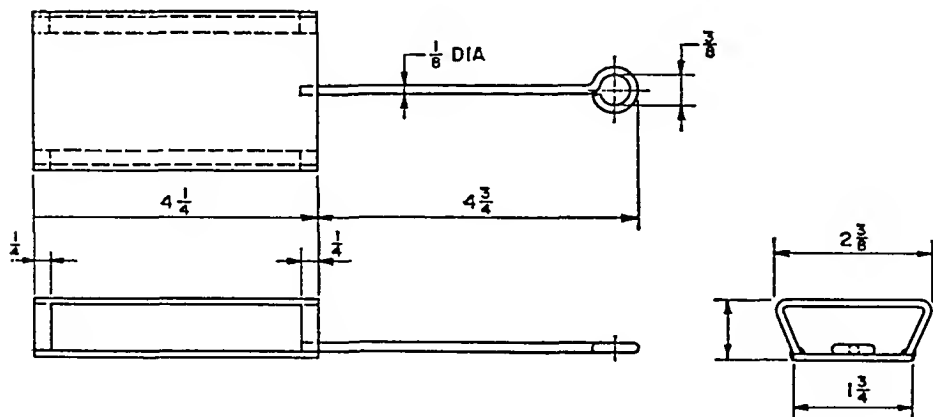


FIG. 41-17. Tray for Abderhalden Oven. (All Dimensions in Inches.)

Determine the wavelengths of maximum and of minimum absorbance. Record the wavelength of maximum absorbance as  $\lambda_1$  and the wavelength of minimum absorbance as  $\lambda_2$ . Calculate a third wavelength  $\lambda_3$  which is exactly the same interval in millimicrons above the maximum (longer wavelength) as the minimum is below it [ $\lambda_3 = \lambda_1 + (\lambda_1 - \lambda_2)$ ]. Measure and record the absorbance readings at the 3 wavelengths

$D_1$  = absorbance at wavelength  $\lambda_1$ ,

$D_2$  = absorbance at wavelength  $\lambda_2$ , and

$D_3$  = absorbance at wavelength  $\lambda_3$

Calculate the absorbance factor,  $K$

$$K = \frac{2D_1 - (D_2 + D_3)}{\text{grams styrene monomer per 100 ml}}$$

**Procedure**—Weigh 1 to 2 g of polystyrene accurately into a 100 ml flask and dissolve in chloroform. Dilute to volume. Transfer a portion of the solution to a 1 cm absorption cell. Measure the absorbance of the solution at the 3 wavelengths determined above. Record the absorbance readings as  $S\lambda_1$ ,  $S\lambda_2$  and  $S\lambda_3$ .

**Calculations**—

$$\text{Grams styrene monomer per 100 ml} = \frac{2S\lambda_1 - (S\lambda_2 + S\lambda_3)}{K}$$

$$\text{Styrene monomer per cent} = \frac{\text{grams styrene monomer}}{\text{grams polystyrene}} \times 100$$

#### STYRENE MONOMER GAS CHROMATOGRAPHIC PROCEDURE (ALTERNATE PROCEDURE)<sup>20</sup>

**Scope**—The gas chromatographic procedure is applicable for the determination of styrene monomer in most types of styrene plastics.

**Apparatus**—Gas Chromatograph—(See p 2041.) The chromatograph column is a 4 ft length of  $\frac{1}{4}$  in 1 D stainless steel tubing packed with 20% Carbowax 20 M alkaline on firebrick (80 to 100 mesh). The packing is a product of Wilkens Instrument and Research Inc. Walnut Creek Calif. Catalog No 0033. The unit is operated at 100°C with helium at 8 lb pressure (41 ml per min).

Micro-syringe 0.00 to 0.05 ml Capacity

**Standardization**—Inject 0.05 ml of a solution containing 25 mg of styrene monomer in a mixture of 10 ml of methylene chloride and 5 ml of methanol into the gas chromatograph. Note the time required for the emergence of the monomer peak. Measure the area of the peak.

**Procedure**—Weigh 1.5 g of polystyrene into a 1 oz bottle and add several glass beads. Pipet 100 ml of methylene chloride into the bottle. Cap the bottle and place in a mechanical shaker until the plastic is dissolved. Precipitate most of the plastic by slowly adding 50 ml of methanol to the solution. Recap the bottle and shake vigorously on the mechanical shaker for 15 min. Centrifuge for 5 min. Inject 0.05 ml of the supernatant liquor into the gas chromatograph. Measure the area of the resulting styrene monomer peak.

<sup>20</sup> Samsel, E. P. The Dow Chemical Co. unpublished data.

## Calculations.—

$$\text{Styrene monomer, milligrams} = \frac{\text{milligrams monomer in standard} \times \text{peak area sample}}{\text{peak area standard}}$$

$$\text{Styrene monomer, per cent} = \frac{\text{milligrams styrene monomer}}{\text{milligrams sample}} \times 100.$$

NOTE.—If a gas chromatograph with a more sensitive detector, such as a flame ionization gauge, is available, the sample may be dissolved in 25 ml. of methylene chloride and a 0.002-ml. aliquot injected directly into the column at a temperature of 130°C.

*POLYETHERS AS SURFACE ADDITIVES*<sup>13</sup>

*Procedure.*—Wash 20.0 g. of the plastic with three 50-ml. portions of boiling ethanol. Combine the extracts in a 250-ml. beaker, and evaporate to dryness on a steam bath. Dissolve the residue in 2 to 3 ml. of water, and transfer to a 50-ml. conical centrifuge tube. Rinse the beaker with water, and transfer to the tube. Use sufficient water to make a total volume of 10 ml. Proceed as directed in the second paragraph of "Calibration," p. 2051.

Calculations.—Read the milligrams of polyether from a previously prepared standard curve.

$$\text{Polyethers, per cent} = \frac{\text{milligrams of polyether}}{\text{weight of sample in milligrams}} \times 100.$$

*MINERAL OIL AS SURFACE ADDITIVE*

*Procedure.*—Extract 200 g. of plastic with three 500-ml. portions of 30° to 60° petroleum ether. Evaporate the extracts on a steam bath to a volume of about 10 ml. Transfer the solution to a 6-in. Babcock milk test bottle. Immerse the bottle in a boiling water bath, and evaporate the solution to dryness. A stream of nitrogen directed into the bottle by means of a 4-in., No. 20 syringe needle will facilitate the evaporation. After all the solvent is removed, place the bottle in an ice bath. Add slowly, with constant swirling, 30 ml. of a 1:1 mixture of concentrated H<sub>2</sub>SO<sub>4</sub> and 30% fuming H<sub>2</sub>SO<sub>4</sub>. After the acid has been added, place the bottle in a water bath at 60°C. for 10 min. Cool the solution to room temperature and add concentrated H<sub>2</sub>SO<sub>4</sub> until the liquid level rises about half-way up the graduated portion of the bottle. Centrifuge the bottle for 6 min. at about 1500 r.p.m.

Calculations.—Determine the volume of the unreacted oil:

$$\text{Mineral oil, per cent} = \frac{\text{milliliters of undissolved layer} \times 0.78 \times 100}{\text{sample weight}}.$$

*ESTER PLASTICIZERS, INFRARED SPECTROMETRIC PROCEDURE*<sup>21</sup>

*Apparatus.* Infrared Spectrometer.—Perkin-Elmer Model 12, with NaCl prism or equivalent.

*Preparation of Standard Curve.*—Weigh 0- to 175-mg. portions of the ester into separate 2-oz., narrow mouth bottles. To each bottle add sufficient reprecipitated polystyrene so that the total weight is 2500 mg. Pipet 50 ml. of carbon tetrachlo-

<sup>21</sup> Kiley, L. R., Anal. Chem., 29, 1895, 1957.

ride into each bottle. Cap the bottles and place them on a mechanical shaker until dissolved. Obtain the infrared spectrum of each solution from about  $5\ \mu$  to  $65\ \mu$ . Draw a base line from  $5.6$  to  $5.8\ \mu$ . Measure the absorbance of the ester peak which occurs at approximately  $5.75\ \mu$ . Plot the analytical curve of absorbance versus percentage.

**Procedure.**—Weigh exactly 25 g of plastic into a 2 oz bottle, and dissolve it in 50 ml of carbon tetrachloride. Obtain the infrared spectrum and measure the absorbance of the ester peak as described above.

**Calculations.**—Calculate the percentage of ester from the analytical curve.

#### FATTY AMIDE SURFACE ADDITIVES<sup>22</sup>

**Procedure.**—Weigh 25.0 g of plastic into flask B (Fig 41 18). Add 50 ml of anhydrous methanol to the flask. Connect the filter tube and flask A to the sample flask. Place the flask on the steam bath and heat until the sample boils gently for 2 min. Immediately reverse the position of the assembly and with the aid of air pressure, filter the methanol into the bottom flask. Remove the top flask and filter tube, and place a 0 to  $100^{\circ}\text{C}$  thermometer into the flask. Allow the methanol solution to cool slowly. Record the temperature when a distinct increase of turbidity is observed.

**Calculations.**—Read the concentration of aliphatic amide (milligrams per 50 ml) from a standard curve previously prepared from data obtained by treating 0 to 20 mg of the amide and 25.0 g of amide free polystyrene in the same way.

$$\text{Fatty amide, per cent} = \frac{\text{milligrams of fatty amide}}{\text{grams of sample} \times 10}$$

#### VISCOSITY OF 10% SOLUTION<sup>23, 24</sup>

**Apparatus.** Viscosimeter.—Modified Ostwald viscosimeter having a capillary diameter of 14 to 15 mm (Capillary A, Fig 41 19). Calibrate at  $25^{\circ}\text{C}$  against National Bureau of Standards standard viscosity oils.

**Mechanical Shaker**

**Electric Timer.** Reading to 0.1 sec

**Constant Temperature Bath.**—Regulate the bath to  $25^{\circ} \pm 0.01^{\circ}\text{C}$

**Reagents.** Toluene.—Redistilled

**Procedure.**—Grind the sample to pass an ASTM No 12 ( $1680\ \mu$ ) screen. Weigh 0.9593 g of the sample into a 2 oz wide mouthed bottle, and add 10 ml of toluene to make a 10% solution of plastic. Place a piece of aluminum foil over the opening of the bottle and screw the cap on tightly. Place the bottle on the shaking machine and agitate until the sample is completely dissolved.

Affix a small piece of cotton to the tip of a 5 ml pipet with a paper clip or wire. Draw sufficient solution through the cotton as a filter and pipet 5 ml into the viscosimeter. Place the viscosimeter in the constant temperature bath at  $25^{\circ} \pm 0.01^{\circ}\text{C}$ . When the solution attains the temperature of the bath, use a rubber bulb to force the liquid 5 to 8 mm above the upper calibration mark. Release the pressure. Using the electric timer measure the time required for the liquid level to pass between the 2 calibration marks. Make triplicate flow time measurements which should check to 0.1 sec.

<sup>22</sup> Kramer, W. R., and Sienger, V. A., The Dow Chemical Co., unpublished data.

<sup>23</sup> Streeter, D. J., The Dow Chemical Co., unpublished manuscript.

<sup>24</sup> ASTM Standards, Pt. 7, D445-53T, ASTM, Philadelphia, 201, 1958.

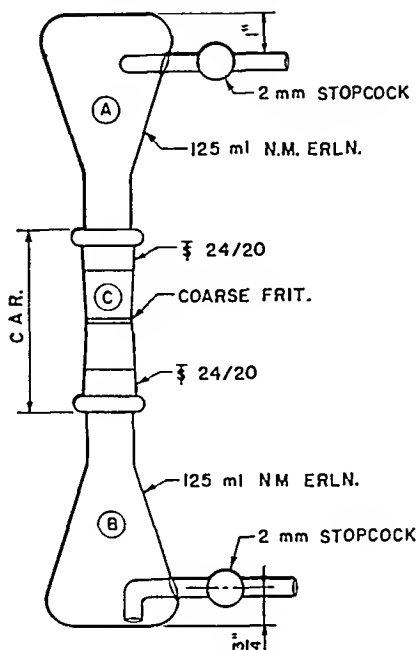


FIG. 41-18. Settling Apparatus for Determining Fatty Amides.

## Calculations.-

$$\text{Absolute viscosity, c.p.s.} = \frac{T_1 \times D_1 \times n}{T_2 \times D_2}$$

where  $T_1$  = time of flow of unknown solution,  
 $T_2$  = time of flow of standard viscosity oil,  
 $D_1$  = density of unknown solution,  
 $D_2$  = density of standard viscosity oil, and  
 $n$  = viscosity of standard viscosity oil in c.p.s.

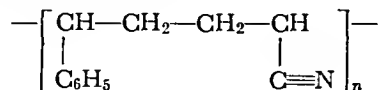
The density of a 10% solution of polystyrene in toluene at 25°C. is 0.8810.

## STYRENE-ACRYLONITRILE COPOLYMERS

Monomers: styrene  $\text{C}_6\text{H}_5\text{CH}=\text{CH}_2$

acrylonitrile  $\text{CH}_2=\text{CHC}\equiv\text{N}$

Copolymer structure:





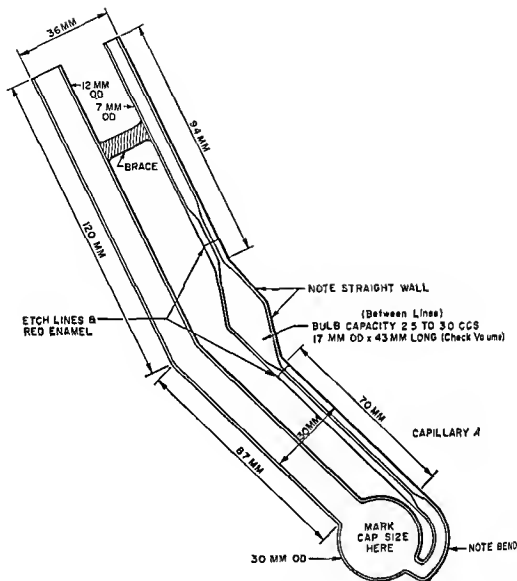


FIG. 41-19 Modified Ostwald Viscosimeter

COMBINED STYRENE <sup>25</sup>

**Apparatus** Ultraviolet Recording Spectrophotometer—Cary Model 11 or equivalent.

**Reagents** Redistilled Tetrahydrofuran

**Procedure** Weigh 100 mg of the additive free plastic into a 100 ml volumetric flask. Dissolve the material in tetrahydrofuran and dilute to volume with the same solvent. Transfer a portion of the solution to a 1.0 cm absorption cell. Record the absorption curve from 300  $m\mu$  to 240  $m\mu$  using the pure solvent as the reference solution. Draw a base line across the absorption minima located at

<sup>25</sup> Meehan E J J Polymer Sci 1, 175 1946 Crummett W B Simek J and Starens C J The Dow Chemical Co unpublished data

250  $m\mu$  and at 267  $m\mu$ . Measure the net absorbance of the maximum at 259  $m\mu$ .

**Calculations.**—Calculate the number of milligrams of combined styrene per 100 ml. from an analytical curve prepared by treating purified polystyrene in the manner described above.

$$\text{Combined styrene, per cent} = \frac{\text{milligrams of combined styrene}}{\text{milligrams of sample}} \times 100.$$

#### TOTAL ACRYLONITRILE <sup>26</sup>

**Scope.**—This method is suitable for determining total nitrogen in nitrogen-containing resins. The method is not applicable for use on materials containing nitro-groups.

**Apparatus.** Kjeldahl Flasks, 800-ml.

Kjeldahl Digestion and Distillation Equipment.

**Reagents.** Sodium Sulfide Solution.—Dissolve 40 g. of  $\text{Na}_2\text{S}$  in distilled water, and dilute to 1 liter.

Sodium Hydroxide Solution.—Dissolve 1000 g. of technical grade  $\text{NaOH}$  in 1 liter of distilled water.

**Procedure.**—Transfer approximately 1 g. of the sample, weighed to the nearest 1 mg., to a Kjeldahl flask. Add 0.5 g. of mercuric oxide, 10 g. of  $\text{K}_2\text{SO}_4$ , and 25 ml. of concentrated  $\text{H}_2\text{SO}_4$ , washing down any particles of sample adhering to the neck of the flask. Mix the contents of the flask and place it on the digestion rack. Heat gently at first and then gradually bring the temperature up to boiling. Turn the flask occasionally to aid in bringing the acid into contact with any undigested material. Continue the digestion for 2 hr. after the solution becomes colorless or nearly so.

Pipet 50 ml. of 0.2  $N$   $\text{HCl}$  into a 500-ml. Erlenmeyer flask, and place it so that the tip of the delivery tube of the condenser dips just below the surface of the solution.

Allow the Kjeldahl flask to cool and add about 500 ml. of water. Mix the solutions thoroughly and cool again. Add 1 to 2 g. of mossy zinc and 25 to 30 ml. of the  $\text{Na}_2\text{S}$  solution. Add 80 to 90 ml. of  $\text{NaOH}$  solution, pouring it slowly down the side of the flask, preventing mixing of the solutions as far as possible. Immediately connect the flask to the connecting bulb and condenser.

Swirl the contents of the flask carefully to mix the solutions. Start to heat immediately and then distill over about 300 ml. of solution. Add several drops of methyl red indicator, and titrate the excess acid with 0.2  $N$   $\text{NaOH}$ .

Make a blank determination, following the same procedure and using the same amounts of all reagents.

**Calculation.**—

$$\text{Acrylonitrile, per cent} = \frac{(A - B)N \times 0.053 \times 100}{C}$$

where  $A$  = milliliters of  $\text{NaOH}$  solution required for titration of the blank,  
 $B$  = milliliters of  $\text{NaOH}$  solution required for titration of the sample,  
 $N$  = normality of the  $\text{NaOH}$  solution, and  
 $C$  = sample weight in grams.

<sup>26</sup> ASTM Standards, Pt. 8, D1013-52, ASTM, Philadelphia, 587, 1958.

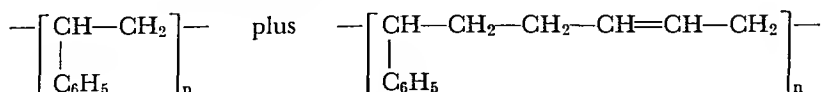
## STYRENE-RUBBER PLASTICS

Styrene-rubber plastics are generally made by blending rubber with polystyrene, or by dissolving the rubber in styrene monomer followed by polymerization. Styrene-rubber plastics consist of at least 50% styrene.

Monomers: styrene  $\text{C}_6\text{H}_5\text{CH}=\text{CH}_2$

butadiene  $\text{CH}_2=\text{CHCH}=\text{CH}_2$

Polymer structure:

VISCOSITY OF 10% SOLUTION <sup>28</sup>

**Apparatus.** Viscosimeter.—Modified Ostwald viscosimeter having a capillary diameter of 1.4 to 1.5 mm. (Capillary A, Fig. 41-19), and calibrated at 25°C. against National Bureau of Standards standard viscosity oils.

**Mechanical Shaker.**

Electric Timer Reading to 0.1 Sec.

Constant Temperature Bath.—Regulated to  $25^\circ \pm 0.01^\circ\text{C}$ .

**Reagents.** Toluene, Redistilled.

**Procedure.**—Weigh exactly 4 g. of the plastic directly into a 2-oz., wide-mouthed bottle containing 15 to 20 g. of bentonite clay. Add exactly 36 g. of toluene. Stopper the bottle with a cork covered with aluminum or tin foil, and shake until the plastic has dissolved. Allow the mixture to stand until the clay and gels have settled out. Determine the viscosity of the clear solution as prescribed in the "Procedure," p. 2060.

DETERMINATION OF BUTADIENE COPOLYMERS  
IN PLASTIC BLENDS <sup>29</sup>

**Scope.**—This method is designed for the determination of butadiene-styrene copolymers in rubber-styrene plastics. It appears suitable also for the determination of most unsaturated polymers or copolymers blended with saturated polymers. The method may also be used to degrade or solubilize unsaturated polymers for the isolation of insoluble fillers.

**Principle.**—The unsaturated polymer is oxidized with the formation of soluble aldehyde fragments. Unattacked polymer is then precipitated by the addition of a nonsolvent and weighed.

**Reagents.** Tertiary-Butyl Hydroperoxide.—Commercial solution containing 60% hydroperoxide and 40% *tert*-butyl alcohol.

Osmium Tetroxide, 0.003 *M* in Benzene.—This reagent is unstable and must be stored in a dark place in a tightly stoppered vessel.

**Procedure.**—Weigh 0.5 g. of the additive-free polymer into each of two 250-ml. beakers containing 50 g. of ortho-dichlorobenzene. Heat on a hot plate at 130°C.

<sup>28</sup> Streeter, D. J., The Dow Chemical Co., unpublished manuscript; ASTM Standards, Pt. 7, D445-53T, ASTM, Philadelphia, 201, 1958.

<sup>29</sup> Kolthoff, L. M., Lee, T. S., and Carr, C. W., J. Polymer Sci., 1, 429, 1946.

until dissolved. Cool the solutions to 80° to 90°C and add 10 ml of the hydrogen peroxide and 1 ml of osmium tetroxide solution to 1 of the beakers. The untreated sample is carried through as the blank. Increase the temperature to 110 to 115°C for exactly 10 min. Copious evolution of gases will occur during this period. Prolonged heating may cause excessive oxidation even of the saturated polymer.

Cool the solutions to room temperature and pour slowly with vigorous stirring into 600 ml of ethanol containing 4 drops of sulfuric acid. Rinse the beaker with 20 ml of benzene. Allow the precipitates to settle 30 min and filter through medium porosity sintered glass crucibles. Wash the residues thoroughly with warm ethanol and then dry in a vacuum oven at 110°C for 4 hr. The difference in weight between the blank and the treated sample is a measure of the rubber content of the sample.

Calculation —

$$\text{Butadiene copolymer, per cent} = \left[ \frac{(A - B)}{A} - \frac{(C - D)}{C} \right] \times 100$$

where  $A$  = weight of the treated sample

$B$  = weight of residue from the treated sample

$C$  = weight of the untreated sample and

$D$  = weight of residue from the untreated sample

#### STYRENE BUTADIENE RUBBER <sup>30</sup>

**Scope**—This method provides for the determination of styrene butadiene rubber in styrene rubber molding and extrusion materials in the range from 0 to 50%.

**Principle**—A known weight of sample is dissolved in carbon disulfide and infrared absorption measurements are made at the wavelength characteristic of trans 1,4 butadiene. The sample absorbance is then compared with those of corresponding standards.

**Apparatus** Infrared Spectrometer—Baird Associates double beam instrument with sodium chloride optics or equivalent.

Infrared Cell 0.7 mm with Sodium Chloride Windows

Sample Shaker—Burrell Wrist Action or equivalent

**Reagents** Carbon Disulfide Infrared Grade

Polystyrene Pure

Rubber—Approximately 70% butadiene 30% styrene

**Preparation of Standard Absorption Curve**—Weigh 2300 mg of pure polystyrene into each of five 2 oz narrow mouthed bottles. (Since 2500 mg samples are used 2300 mg of pure polystyrene represents 92% the typical polystyrene content of many styrene rubber plastics. Additives usually total about 8%.) Weigh 25, 75, 125, and 175 mg portions of rubber into the 2 oz bottles. Pipet 50 ml of carbon disulfide into each of the bottles. Place the bottles on the shaker until the solids are completely dissolved. Obtain the infrared spectrum of each standard solution from 8.5 to 12  $\mu$  in the 0.7 mm cell. Measure the absorbance of each solution at 10.3  $\mu$  employing the base line from 10.1 to 10.6  $\mu$ .

Plot analytical and interference curves of absorbance versus percentage composition. The absorbance of the polystyrene blank solution at the indicated wavelength represents 0% component since the blank as prepared compares with a

<sup>30</sup> Scheddel R. The Dow Chemical Co. unpublished manuscript.

sample of 92% polystyrene content. Most samples are 90 to 94% polystyrene, so no significant error is introduced by using a background of 92% polystyrene.

**Procedure.**—Weigh 2500 mg. of sample into a 2-oz., narrow-mouthed bottle. Pipet 50 ml. of carbon disulfide into the bottle. Place the bottle on the shaker until the sample is dissolved. (If pigment is present, it will not dissolve but will go into suspension and will not interfere with the analysis.)

Scan the solution in the 0.7-mm. cell over the wavelength range from 8.5 to 12  $\mu$ , using the infrared spectrometer.

**Calculations.**—Measure the absorbance at 10.3  $\mu$ , employing the base line from 10.1 to 10.6  $\mu$ . Determine the percentage of rubber from the measured absorbance by graphical solution, employing all necessary interference corrections.

To obtain the percentage of butadiene, multiply the percentage of rubber found by the butadiene content of the standard rubber. If the butadiene composition of the rubber used in samples is not the same as that used in standards, the approximate rubber composition in the sample may be calculated by multiplying the result obtained by graphical solution by:

$$\frac{\text{percentage of butadiene in standard rubber}}{\text{percentage of butadiene in sample rubber}}$$

#### DETERMINATION OF TOTAL UNSATURATION<sup>31</sup>

**Scope.**—This method is suitable for determining total unsaturation in plastics containing polybutadiene, butadiene copolymers, and natural rubber.

**Principle.**—Unsaturation is determined by addition of iodine monochloride at double bonds in the polymer chains, as measured by titration.

**Reagents.** Iodine Monochloride, 0.1 *N*.—Dissolve 3.2 g. of iodine trichloride and 1.4 g. of iodine in 1 liter of carbon tetrachloride.

**Procedure.**—Add 0.1 to 1.0 g. of the additive-free plastic, depending upon the degree of unsaturation, to 50 ml. of melted *p*-dichlorobenzene in a 500-ml. iodine flask. Heat to 175° to 180°C., and maintain this temperature until solution is complete. Allow the solution to cool slightly and add 50 ml. of chloroform. When the solution has reached room temperature add 50 ml. of 0.1 *N* iodine monochloride. Stopper the flask and allow to stand for exactly 1 hr. at room temperature in the dark. Add 25 ml. of 15% potassium iodide solution, 50 ml. of water and 100 ml. of ethanol. Titrate the liberated iodine with 0.1 *N* sodium thiosulfate. Carry a reagent blank through the same procedure.

**Calculations.**—

$$\text{Butadiene, per cent} = \frac{\text{Net milliliters of 0.1 } N \text{ I}_2 \times 0.271}{\text{sample weight}}$$

#### 2,6-di-*tert*-BUTYL-*p*-CRESOL<sup>32,33</sup>

**Scope.**—This method is intended for the determination of 2,6-di-*tert*-butyl-*p*-cresol or similar phenolic-type stabilizers in plastics.

**Apparatus.** Spectrophotometer.—Beckman Model B, or its equivalent.

<sup>31</sup> Kemp, A. R., and Peters, H., *Anal. Chem.*, 15, 453, 1943.

<sup>32</sup> Lovestrom, E. F., and Cobler, J. G., The Dow Chemical Co., unpublished data.

<sup>33</sup> Mehlenbacher, V. C., *The Analysis of Fats and Oils*, Garrand Press, Champaign, Illinois, 1960.

**Reagents** Dioxane Purified—Add an excess of sodium hydroxide to the dioxane allow to stand for 24 hr and distill

**Ferric Chloride Solution**—Dissolve 200 mg of ferric chloride ( $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ ) in 100 ml of distilled water Prepare fresh daily

**2,2 Bipyridine Solution**—Dissolve 200 mg of 2,2 bipyridine in 0.5 ml of ethanol and dilute to 100 ml with water

**Calibration Curve**—Prepare a standard solution containing 0.05 mg of 2,6-di-*tert*-butyl *p*-cresol (DTBC) per milliliter of 2B absolute ethanol Transfer 1 to 5 ml of the standard solution to 100 ml volumetric flasks Prepare an additional flask to use as a reagent blank

To each flask add 10 ml of the  $\text{FeCl}_3$  solution and 10 ml of the bipyridine solution Dilute to volume with 1:1 ethanol water solution Allow the solutions to stand for 35 min in the dark Transfer a portion of each solution to a 1 cm absorption cell Read the absorbance using the reagent blank as the reference solution

Plot the absorbances of the standard solutions against the number of milligrams of DTBC per 100 ml of solution on rectangular coordinate paper

**Procedure**—Accurately weigh about 0.10 g of the polystyrene sample in a 2-oz bottle and dissolve in 10 ml of purified dioxane Slowly add 40 ml of 2B absolute alcohol from a buret to precipitate the polystyrene Place the bottle on a shaker and shake for about 10 min Centrifuge the mixture for 10 min to settle the polymer Pipet a 10 ml aliquot of the clear solution into a 100 ml volumetric flask and treat as described in the second paragraph of Calibration Curve immediately above

**Calculations**—Convert the absorbance reading of the sample solution to the number of milligrams of DTBC by means of the standard curve

$$2,6\text{-di-}t\text{-butyl } p\text{-cresol per cent} = \frac{\text{milligrams found in aliquot} \times 100}{\text{milligrams of sample in aliquot}}$$

## VINYL CHLORIDE PLASTICS

Vinyl chloride plastics are based on resins made by the polymerization of vinyl chloride or the copolymerization of vinyl chloride with other unsaturated compounds The more common vinyl chloride copolymers are those containing vinyl acetate acrylates vinylidene chloride or acrylonitrile

### POLYVINYL CHLORIDE

Monomer vinyl chloride  $\text{CH}_2=\text{CHCl}$

Polymer structure  $-\text{[CH}_2-\text{CHCl]}-\text{n}$

### VOLATILE MATERIAL <sup>34</sup>

**Principle**—The loss in weight after 4 hr exposure in a vacuum oven at 113.5°C is reported as percentage volatile

**Apparatus** Vacuum Oven—Aberhalden type employing 1,1,2 trichloroethane <sup>35</sup> the heat transfer liquid (Fig 41.16)

Desiccator

<sup>34</sup> Gillard E. J. The Dow Chemical Co unpublished manuscript

*Procedure.*—Accurately weigh about 5 g. of plastic into a tared, flat bottom, evaporating dish. Place the dish in a vacuum oven for 4 hr. at 113.5°C. and 10 to 20 mm. Hg pressure.

Remove the sample from the oven. Cool in a desiccator and reweigh.

Calculation.—

$$\text{Volatile, per cent} = \frac{\text{grams loss in weight}}{\text{grams of sample}} \times 100$$

#### MOISTURE<sup>34</sup>

*Reagents.* Sodium Tartrate ( $\text{Na}_2\text{C}_4\text{H}_4\text{O}_6 \cdot 2\text{H}_2\text{O}$ ).—Reagent grade, Mallinckrodt. This reagent contains  $15.66 \pm 0.05\%$  water.

*Solution W, Water-in-Methanol Standard.*—Pipet 2.5 ml. of water into a 1-liter volumetric flask. Dilute to the mark with anhydrous methanol and mix well.

*Karl Fischer Reagent.*—This can be obtained from laboratory supply houses. It is prepared as follows: (1) dissolve 127 g. of finely granulated iodine in 1200 ml. of anhydrous methanol (less than 0.05% water) contained in a 2-liter, brown, glass-stoppered bottle. Add 395 g. of anhydrous pyridine, and mix thoroughly; (2) connect a sulfur dioxide cylinder to the reagent bottle through a 1-gal. bottle arranged as a trap. Use glass delivery tubing with rubber connectors; (3) place the reagent bottle on a large solution balance, and add 95 g. of sulfur dioxide in small increments. Cool the solution. Dilute to volume with methanol and mix thoroughly. This reagent loses strength gradually; it must be standardized daily.

*Apparatus.*—Any suitable Karl Fischer apparatus for water determinations, including automatic, 25-ml. burets of a type that minimizes errors due to reaction of the reagents with atmospheric moisture (see ASTM D1123-54). Optionally, an instrument for detection of the "dead-stop" end point, such as the Beckman Aquameter, may be used.

*Standardization of Reagents.*—Add exactly 10 ml. of Fischer reagent to the titration vessel, and back-titrate with solution W. Repeat several times and compute the average equivalence ratio.

$$F_a = \frac{\text{milliliters of Fischer reagent}}{\text{milliliters of solution W}}$$

The equivalence ratio,  $F_a$ , should be adjusted to between 0.7 and 1.3 by addition of water or methanol to solution W.

Accurately weigh about 1 g. of reagent grade sodium tartrate, and transfer it to the titration vessel. Titrate with Fischer reagent to an excess of about 2 ml. Back-titrate with solution W. Compute the water equivalence in grams of water per milliliter of Fischer reagent:

$$F_f = \frac{(\text{grams of sodium tartrate}) \times 0.1566}{(\text{milliliters of Fischer reagent}) - F_a(\text{milliliters of solution W})}$$

*Procedure.*—Weigh 5 g. of plastic to the nearest 0.01 g. Transfer to the titration vessel and add then 10 ml. of Fischer reagent. Stir continuously for 10 min. Depending on the design of the titration vessel used, excessive moisture may be picked up from the air if the stirring period is permitted to exceed 10 min. Back-titrate with solution W.

## Calculation —

$$\text{Moisture, per cent} = \frac{(\text{milliliters of } A) - F_0(\text{milliliters of solution } W)}{\text{gram of sample}} \times F_1 \times 100$$

where  $A$  = Fischer reagent

**DRY SIEVE ANALYSIS<sup>25</sup>**

**Principle**—A sample of the plastic is mixed with talc (lubricant) and is placed on a 50-mesh sieve. After twenty minutes of shaking the percentage retained on the screen is reported.

**Apparatus** Sieve—Standard 50 mesh and pan

**Mechanical Sieve Shaker**—A shaker such as Rotap Cat No S-74715 E. I. Sargent and Co

**Talc**—Finer than 200 mesh

**Procedure**—Weigh 100 g of plastic into a 400 ml beaker and add 10 g of talc. Mix the talc and plastic thoroughly. Obtain the tare weight of the 50 mesh sieve. Attach the pan, add the plastic mixture and mount in the mechanical sieve shaker. Run the shaker for 20 min. Reweigh the 50 mesh sieve.

**Calculation**—Report the gain in weight as the percentage retained on the 50-mesh sieve.

**INORGANIC CHLORIDE<sup>26</sup>**

**Principle**—The chloride is extracted from the resin with water and titrated amperometrically with 0.001 N silver nitrate.

**Apparatus** Amperometric Assembly—See Fig. 41-20

**Micro Buret**, 5 ml

**Reagents** Alcohol, Formula 30—Distill Formula 30 alcohol discarding the first and last 10% fractions.

**Silver Nitrate Solution** 0.001 N—Dissolve 16.99 g of pure silver nitrate in water and dilute to 1000 ml. Dilute 10.00 ml of this stock solution to 1000 ml with water.

**Gelatin**, 0.1%—Dissolve 0.1 g of gelatin in water and dilute to 100 ml. Prepare fresh daily.

**Acetone**—Chloride free

**Procedure**—Weigh 10 g of the finely divided plastic into a 250 ml Erlenmeyer flask. Add 75 ml of boiling distilled water. Cover the flask with a watch glass and place it on a steam bath for 5 min. Remove the flask, cool and allow the resin to settle. Filter the water through Whatman No. 41 H filter paper into a 100 ml volumetric flask. Wash the resin with 25 ml of water and transfer to the filter. Dilute the filtrate to volume and transfer a 50 ml aliquot to a 100-ml beaker.

Add 1 ml of 0.1% gelatin solution, 50 ml of chloride free acetone and 0.2 ml of concentrated nitric acid. Titrate amperometrically with 0.001 N silver nitrate solution with a potential of about 0.5 v applied across the platinum electrodes. Add the silver nitrate in 0.1 ml increments recording the microammeter reading.

<sup>25</sup> Gillard, E. J. The Dow Chemical Co., unpublished manuscript.

<sup>26</sup> Kolthoff, I. M., and Lingane, J. J. *Polarography*, Vol. II, 2nd Ed., Interscience Publishers Inc., New York, 1952.



after each addition. Add sufficient silver nitrate to give 1 to 2 ml. in excess as noted by the increased ammeter readings.

Calculation.—Plot the number of milliliters of 0.001 *N* silver nitrate solution on the X-axis of a graph paper against the corresponding microampere readings on

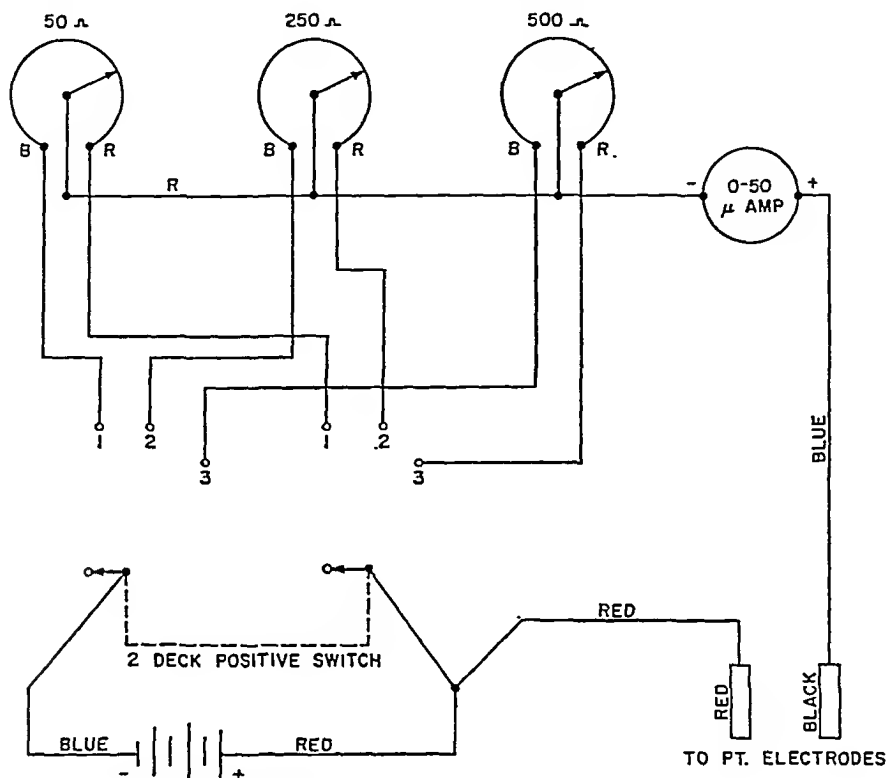


FIG. 41-20. Wiring Diagram for Amperometric Titrator.

the Y-axis. Draw straight lines through the points representing the 2 slopes produced. The point of intersection gives the number of milliliters of silver nitrate used to react with the chloride. Run a blank through the entire procedure and subtract it from the sample titration.

$$\text{Chloride, per cent} = \frac{\text{milliliters} \times N \times .0355}{\text{sample weight in aliquot}} \times 100$$

#### IVET SIEVE ANALYSIS<sup>37</sup>

**Principle.**—A slurry of the resin in a dilute wetting agent solution is poured onto a sieve. The fine particles are washed through with a gentle stream of water. The wet sieve technique eliminates static charges that cause resin particle agglom-

<sup>37</sup> ASTM Supplement to ASTM Standards, Pt. 9, D1705-59T, ASTM, Philadelphia, 97, 1959.

eration A wetting agent promotes the complete displacement of air in porous resins

**Apparatus** Sieves.—U S Standard 8 in sieves as required (the minimum sieve size must be U S No 325  $44\ \mu$ , or larger)

Oven—Circulating air type oven operating at  $70^\circ \pm 2^\circ\text{C}$

**Reagent** Sodium Lauryl Sulfate—Or any sodium alkyl aryl sulfonate, 0.5% aqueous solution

**Procedure.**—Weigh the sieves to the nearest 0.1 g and assemble them in order of increasing number from top to bottom Transfer to a beaker, a sample of not less than 25 g nor more than 100 g weighed to the nearest 0.1 g Use a sample of such size that not more than 20 g remains on any one sieve Add approximately 300 ml of the wetting agent solution to the beaker and stir until the resin is thoroughly wetted

Pour the slurry on the top sieve Complete the transfer of resin using additional wetting agent solution Wash the fine particles through with a gentle stream of water Remove the top sieve and continue washing each successive sieve If the particles on the lower sieves are not thoroughly wet, add additional wetting agent solution to the sieve

Dry the washed sieves containing the resin at  $70^\circ \pm 2^\circ\text{C}$  and weigh

Calculations—Determine the residue on each sieve by weight difference

### TOTAL CHLORINE<sup>38 39</sup>

**Scope**—This method is suitable for determining total chlorine in vinyl chloride and vinylidene chloride polymers and copolymers

**Apparatus** Parr Peroxide Bomb—Series 2100, 22 ml and accessories

Blast Burner

Safety Shield

**Reagents** Ferric Nitrate Solution.—Dissolve 50 g of  $\text{Fe}(\text{NO}_3)_3$  in distilled water and dilute to 1 liter

Nitric Acid 1:1.—Dilute 1 volume of  $\text{H}_2\text{O}$  with 1 volume of concentrated  $\text{HNO}_3$

**Procedure**—Dry the finely powdered sample for 45 min in an oven at  $100^\circ\text{C}$  in an atmosphere of nitrogen Place the sample in a desiccator until cool Weigh about 0.2 g of the dry sample accurately into a fusion cup Add 0.50 g of dry powdered sugar and 15 g of  $\text{Na}_2\text{O}_2$  Assemble the bomb, making sure the head gasket is in place, and tighten with a wrench Shake the bomb vigorously to mix the contents Tap the bomb lightly on the bench to dislodge any particles sticking to the upper portions of the bomb

Set the bomb over the hole in the ignition housing stand, and place a safety shield in front of the assembly Apply a sharp intense flame to the bottom of the bomb Heat until a dark red spot appears on the side of the bomb Underheating will result in incomplete oxidation of the organic matter and low chlorine results<sup>40</sup> Allow the bomb to cool in air for several minutes and then to cool to room temperature under tap water Remove the screw caps taking care to not disturb the bomb lid Wash the outside of the bomb with distilled water

Remove the bomb lid and wash any adhering particles into a 600 ml beaker

<sup>38</sup> ASTM Standards, Pt 9, D1303-55 ASTM, Philadelphia, 517, 1958

<sup>39</sup> Parr Manual Number 121, Peroxide Bomb Apparatus and Methods, Parr Instrument Company, Moline, Illinois, 1950

<sup>40</sup> Caution—Overheating may cause possible damage to the fusion cup and even an explosion

Place the cup on its side in the beaker, add sufficient water to cover about one-third of the bomb, and immediately cover the beaker with a watch glass. When the reaction has completely subsided, remove the cup and wash thoroughly with a stream of water. Neutralize the solution by adding 50 ml. of 1:1  $\text{HNO}_3$  slowly with constant stirring, using care to avoid loss by spattering or overheating.

Add an additional 10 ml. of 1:1  $\text{HNO}_3$ , 2 ml. of nitrobenzene, and 50.0 ml. of 0.1  $N$   $\text{AgNO}_3$ . Stir vigorously until the precipitated  $\text{AgCl}$  becomes a spongy mass. Add 10 ml. of  $\text{Fe}(\text{NO}_3)_3$  indicator and titrate the excess  $\text{AgNO}_3$  with 0.1  $N$  ammonium thiocyanate to the first pink end point. Run a blank determination on the reagents.

Calculation.—

$$\text{Vinyl chloride, per cent} = \frac{[(A \times N_A) - (B \times N_B)] \times .06246}{\text{weight of sample}} \times 100$$

where  $A$  = net milliliters of  $\text{AgNO}_3$  solution,

$N_A$  = normality of  $\text{AgNO}_3$  solution,

$B$  = net milliliters of ammonium thiocyanate solution, and

$N_B$  = normality of ammonium thiocyanate solution.

#### VISCOSITY OF 2% SOLUTION <sup>41</sup>

**Scope.**—This method describes a test procedure for the determination of the dilute solution viscosity of vinyl chloride resins in orthodichlorobenzene at 120°C. To determine the inherent viscosity in cyclohexanone solvent, or the specific viscosity in nitrobenzene solvent, the methods prescribed in *Tentative Method of Test for Dilute Solution Viscosity of Vinyl Chloride Polymers* should be followed.<sup>42</sup>

**Apparatus.** Viscosimeter.—Modified Ostwald viscosimeter, having a capillary diameter of about 0.40 mm. (Capillary A, Fig. 41-19) and calibrated against National Bureau of Standards standard viscosity oils.

**Constant Temperature Oil Bath.**—Maintained at 120°C.

**Constant Temperature Bath.**—Maintained at 165°C.

**Electric Timer.**—Reading to 0.1 sec.

**Reagent.** *o*-Dichlorobenzene, 99.6% pure.

**Procedure.**—Weigh exactly 0.2663 g. of the sample into a 20- by 150-mm. test tube. Add by pipet exactly 10 ml. of *o*-dichlorobenzene, using the solvent to wash down the sides of the test tube. Place the tube in a 165°C. constant temperature bath for 5 min. Use a stirring rod to hasten solution of the particles that may stick to the sides and bottom of the tube. If the sample turns dark, indicating decomposition, it should be discarded.

Suspend a viscosimeter in the 120°C. constant temperature bath for a sufficient time to reach the bath temperature. Affix a small piece of cotton to the tip of a preheated, 5-ml. pipet with a paper clip or wire. Draw sufficient solution through the cotton as a filter and pipet 5 ml. into the viscosimeter. Allow at least 5 min. for temperature equilibrium. Use a rubber bulb to force the liquid 5 to 8 mm. above the upper calibration mark. Release the pressure and, using the electric timer, measure the time required for the liquid level to pass between the 2 calibration marks. Make triplicate flow-time measurements, which should agree within 0.3 sec.

<sup>41</sup> Gillard, E. J., The Dow Chemical Co., unpublished manuscript.

<sup>42</sup> ASTM Standards, Pt. 9, D1243-58T, ASTM, Philadelphia, 530, 1958.

Drain the viscosimeter tube and rinse it immediately with boiling hot *o*-dichlorobenzene. Cool, rinse with acetone and dry.

Calculation —

$$\text{Absolute viscosity, cps} = \frac{T_1 \times D_1 \times \pi}{T_2 \times D_2}$$

where  $T_1$  = time of flow of unknown solution,

$T_2$  = time of flow of standard viscosity oil,

$D_1$  = density of unknown solution,

$D_2$  = density of standard viscosity oil, and

$\pi$  = viscosity of standard viscosity oil in cps

### SHORT TIME STABILITY AT ELEVATED TEMPERATURES<sup>43</sup>

**Scope**—This procedure is suitable for determining the short time stability at elevated temperatures of plastics containing chlorine.

**Apparatus**—Stability Apparatus—Consisting of preheater coil, sample flask, and absorption tube (Fig. 41-21).

**Constant Temperature Bath**—Controlled at  $180^\circ \pm 2^\circ\text{C}$ .

**Procedure**—Cut or shred the sample into pieces so that one dimension is no larger than  $\frac{1}{16}$  in. Spread 10.0 g of the sample evenly upon the bottom of the sample flask. Add 40.0 ml of 0.1 N chloride free NaOH to the absorption tube. Place the sample flask in the constant temperature bath so that it is immersed in the heating medium to within 3 cm of the top. Immediately assemble the apparatus as shown in the

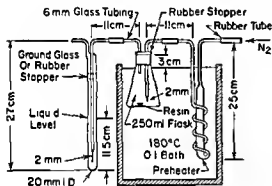


FIG. 41-21. Apparatus for Short Time Stability Test.

diagram (Fig. 41-21). Pass nitrogen gas through the system for exactly 30 min. Control the rate of flow so that 2 to 4 bubbles per sec. will pass through the absorbing tube.

Transfer the contents of the absorbing tube quantitatively to a 250 ml Erlenmeyer flask and acidify with concentrated  $\text{HNO}_3$ . Add 2 ml of nitrobenzene and 50.0 ml of 0.02 N  $\text{AgNO}_3$ . Shake the flask until the precipitated  $\text{AgCl}$  becomes a spongy mass. Add 10 ml of a 5% aqueous solution of  $\text{Fe}(\text{NO}_3)_3$  and titrate the excess  $\text{AgNO}_3$  with 0.02 N ammonium thiocyanate to the first pink end point. Run a blank determination on the reagents.

Calculation —

$$M = (A - B) \times 3.65$$

where  $M$  = short time stability expressed as milligrams of HCl evolved per gram of sample,

$A$  = net milliliters of  $\text{AgNO}_3$  required for sample, times normality, and

$B$  = net milliliters of ammonium thiocyanate times normality.

<sup>43</sup> ASTM Standards, Pt. 9, D793-59, ASTM, Philadelphia, 521, 1959.

## SOLVENT-SOLUBLE EXTRACT

*Scope.*—This method describes a test procedure for the determination of plasticizers and other solvent-soluble organic additives in polyvinyl chloride.

*Apparatus.* Soxhlet Extractor.

Soxhlet Extraction Thimbles.

*Procedure.*—Weigh approximately 5 g. of the finely subdivided plastic accurately into a Soxhlet extraction thimble. Place the thimble in the extractor. Add 2B absolute ethanol to a tared extraction flask. Assemble the apparatus and extract for 24 hr. Allow the extractor to cool, remove the flask, and evaporate the solvent to dryness on a steam bath. Place the flask in a vacuum oven at 70°C. for 1 hr. Remove the flask from the oven and cool in a desiccator. Weigh the flask and contents.

*Calculation.*—

$$\text{Solvent-soluble, per cent} = \frac{\text{weight of extract}}{\text{weight of sample}} \times 100$$

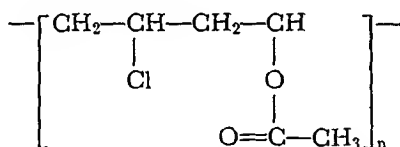
## VINYL CHLORIDE-VINYL ACETATE COPOLYMERS

Description

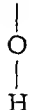
Monomers: vinyl chloride  $\text{CH}_2=\text{CHCl}$

vinyl acetate  $\text{CH}_2=\text{CHOCOCH}_3$

Copolymer structure:



Vinyl chloride-vinyl acetate copolymers frequently contain minor amounts of vinyl alcohol ( $-\text{CH}_2-\text{CH}-$ ) or maleic acid ( $-\text{CH}=\text{CH}-$ ).

DETERMINATION OF POLYVINYL CHLORIDE AND  
POLYVINYL ACETATE IN BLENDS <sup>44</sup>

*Procedure.*—Dissolve 1 g. of the plastic in 15 ml. of redistilled *o*-dichlorobenzene, warming slightly if necessary. Add 100 ml. of warm 96% ethanol slowly with stirring. Reflux the mixture for 2 hr. on a steam bath. Allow the mixture to cool to room temperature and filter through a tared, medium-porosity, sintered-glass crucible. Rinse the precipitate with three 20-ml. portions of a 1:3 ethyl ether:ethanol solution. Dry the crucible and contents to constant weight in a vacuum oven at 70°C. Record the net weight of the precipitate as *A*.

Combine the filtrate and the washings, and evaporate almost to dryness on a steam bath. Dissolve the residue in 30 ml. of acetone and add 10 ml. of  $\text{H}_2\text{O}$

<sup>44</sup> Taat, W. J., and Neul, W. vander, Chem. Weekblad., 44, 393, 1948.

dropwise with stirring. Filter the mixture through a tared, medium porosity, sintered glass crucible. Wash the precipitate with three 5 ml portions of a 4:1 acetone  $H_2O$  solution. Dry the crucible and contents in a vacuum at  $70^\circ C$ . Record the net weight of the precipitate as *B*.

Combine the filtrate and washings in a beaker, and evaporate almost to dryness on a steam bath. Transfer the beaker and contents to a vacuum desiccator, and dry to constant weight (16 to 24 hr). Record the net weight of the residue as *C*.

Calculations.—

$$\text{Polyvinyl chloride, per cent} = \frac{A}{\text{weight of sample}} \times 100$$

$$\text{Polyvinyl acetate, per cent} = \frac{B}{\text{weight of sample}} \times 100$$

$$\text{Plasticizer, per cent} = \frac{C}{\text{weight of sample}} \times 100$$

#### VINYL ALCOHOL<sup>45</sup>

**Reagents** Acetic Anhydride Pyridine Reagent.—Add 60 g of cp acetic anhydride to 440 g of freshly distilled pyridine. Store in a brown, glass stoppered bottle. Prepare fresh weekly.

**Pyridine Water Solution**—Add 8 ml of distilled water to 92 ml of freshly distilled pyridine.

**Potassium Hydroxide, 0.5 *N***—Dissolve 33 g of potassium hydroxide in 200 ml of anhydrous methanol. Add 20 ml of Tergitol 4. Dilute the solution to a volume of 1 liter with freshly distilled pyridine, and store in a brown glass stoppered bottle. Standardize against benzoic acid.

**Procedure**—Weigh 2 to 3 g of sample into a 200 ml pressure bottle containing 20.0 ml of acetic anhydride pyridine reagent. Wash down the neck of the bottle with 35 ml of pyridine. Stopper the bottle. Place the bottle on a steam bath behind a safety shield. Swirl the bottle frequently until the plastic is dissolved. Allow the bottle to remain on the steam bath for 20 min after complete solution.

Remove from the steam bath and allow to cool to room temperature. Add 25 ml of the pyridine water solution. Stopper the bottle and swirl gently to mix the contents. Place the bottle on the steam bath for 30 min. Remove the bottle from the bath and allow it to cool to room temperature. Wash down the sides of the bottle with 25 ml of pyridine. Cool the bottle in an ice bath at  $0^\circ C$  for 15 min. Titrate to a phenolphthalein end point with 0.5 *N* KOH. Run a blank on the reagents following the same procedure.

Calculation—

$$\text{Vinyl alcohol, per cent} = \frac{(A - B) \times N \times 0.440}{\text{grams of sample}} \times 100$$

where *A* = milliliters of KOH used for blank,

*B* = milliliters of KOH used for sample, and

*N* = normality of KOH.

<sup>45</sup> Kennett, C. J., in Kline, Gordon M. (ed), *Analytical Chemistry of Polymers*, Part I, Interscience Publishers, Inc., New York, 481-2, 1959. Reproduced with permission.

## MALEIC ACID

**Reagents.** Potassium Hydroxide, 0.1 *N*.—Methanolic solution.

**Ethylene Dichloride.**—Neutralize to phenolphthalein end point with 0.1 *N* methanolic KOH.

**Procedure.**—Weigh 5 g. of sample accurately into a 250-ml. Erlenmeyer flask, and dissolve in 150 ml. of ethylene dichloride. Solution may be hastened by warming to 60° to 70°C. with gentle swirling. Cool the flask and contents to room temperature and titrate to the phenolphthalein end point with 0.1 *N* KOH.

**Calculation.**—

$$\text{Maleic acid, per cent} = \frac{\text{milliliters of KOH} \times N \times .058}{\text{grams of sample}} \times 100$$

TOTAL VINYL ACETATE<sup>46</sup>

**Scope.**—This method is suitable for the determination of vinyl acetate in its copolymers. The procedure measures the sum of the monomeric and polymerized vinyl acetate.

**Principle.**—The copolymer is pyrolyzed under vacuum. The pyrolysis products are dissolved in water and an aliquot is injected into a gas chromatography apparatus. The peak area produced by the acetic acid formed during the pyrolysis is compared with that produced by known amounts of acetic acid.

**Apparatus.** Pyrolysis Tube.—Vycor, see Fig. 41-22.

**Heating Block.**—See Fig. 41-23. The block may be heated with a Meker burner or in a tube furnace.

**Gas Chromatograph.**—Beckman GC-2A or equivalent, with hydrogen flame detector.

**Column,** ¼ in. I.D.—Stainless steel tubing, 4-ft. length, packed with 20% Tween 80 on firebrick (80 to 100 mesh).

**Micro-Syringe,** 0.0 to 10.0 µl.

**Reagents.** Compressed Gases, see "Operating Conditions for Gas Chromatograph," below.

**Acetic Acid,** Glacial.

**Operating Conditions for Gas Chromatograph.**—(a) Helium gas pressure, 40 p.s.i. (120 ml. per min.); (b) compressed air pressure, 16 p.s.i.; (c) hydrogen gas pressure, 7 p.s.i.; (d) column temperature, 100°C.; (e) attenuator, 5 × 10<sup>2</sup>; (f) recorder, 0 to 1 mv.

**Standardization.**—Place about 20 ml. of H<sub>2</sub>O in a 50-ml. volumetric flask and weigh. Add about 400 mg. of glacial acetic acid to the flask, stopper, and reweigh. Dilute to volume with H<sub>2</sub>O. By means of a micro-syringe, inject 3 µl. of the standard solution into the gas chromatographic apparatus.

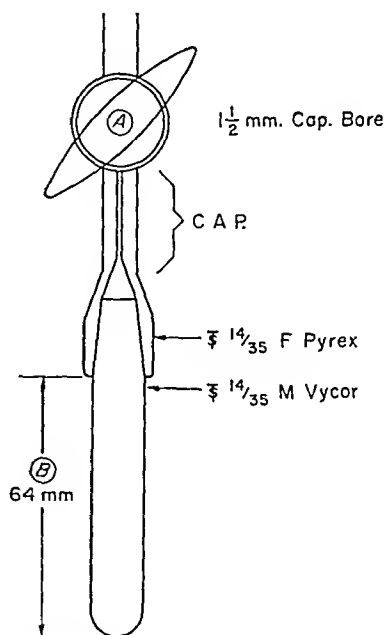


FIG. 41-22. Pyrolysis Tube for the Thermal Decomposition of Polyvinyl Acetate.

<sup>46</sup> Lovestrom, E. F., Miller, D. L., and Cobler, J. G., The Dow Chemical Co., unpublished manuscript.

## VINYLIDENE CHLORIDE PLASTICS

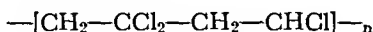
Vinylidene chloride plastics are based on resins made by the polymerization of vinylidene chloride or the copolymerization of vinylidene chloride with minor amounts (not over 50%) of other unsaturated compounds. The common vinylidene chloride plastics are the copolymers with vinyl chloride or acrylonitrile.

## VINYLIDENE CHLORIDE/VINYL CHLORIDE COPOLYMERS

Monomers: vinylidene chloride  $\text{CH}_2=\text{CCl}_2$

vinyl chloride  $\text{CH}=\text{CHCl}$

Copolymer structure:

MOISTURE <sup>47</sup>

Determine the moisture content of the sample as prescribed under "Moisture," p. 2069.

SIEVE ANALYSIS <sup>47</sup>

*Principle.*—A sample of the resin is shaken on a nest of screens. The fractions remaining on each screen and on the pan are weighed and reported by percentage.

*Apparatus.* Screens.—Tyler mesh, numbers 16, 20, 32, 42, 60, 80, 100, 150, 200, pan and cover.

Shaker.—Newark "End Shake" testing sieve shaker, or equivalent; Newark Wire Cloth Company, Newark 14, New Jersey.

Talc.—Finer than 200-mesh.

*Procedure.*—Obtain the tare weights of each of the screens and of the pan. Place exactly 100.0 g. of resin on the 16-mesh screen, and add exactly 10 g. of talc. Shake for 10 min.

*Calculation.*—Weigh the screens and pan. Subtract the tare weights and report the difference as percentage on each screen and percentage on the pan. Subtract 10.00 from the weight of polymer on the pan as a correction for the talc.

## VINYLIDENE CHLORIDE IN VINYLIDENE CHLORIDE-VINYL CHLORIDE COPOLYMERS

Determine the total chloride content of the dry, additive-free resin as prescribed under "Total Chlorine," p. 2072.

$$\text{Vinylidene chloride, per cent} = \frac{\text{percentage of chloride} - 56.73}{0.1641}$$

VISCOSITY OF 2% SOLUTION <sup>48</sup>

The test is carried out in the same way as for polyvinyl chloride; see p. 2073.

<sup>47</sup> Meeks, M. R., The Dow Chemical Co., unpublished manuscript.

<sup>48</sup> ASTM Standards, Pt. 9, D729-57, ASTM, Philadelphia, 29, 1958.



## ETHYLENE PLASTICS

Ethylene plastics are based on resins made by the polymerization of ethylene or copolymerization of ethylene with other unsaturated compounds

## POLYETHYLENE

Monomer ethylene  $\text{CH}_2=\text{CH}_2$

Polymer structure  $-\text{[CH}_2-\text{CH}_2\text{]}_n$

Polyethylenes are currently classified by the ASTM in 3 categories with respect to density

Type I	Low density	0.910–0.925
Type II	Medium density	0.926–0.940
Type III	High density	0.941–0.965

Although the density is a function of the molecular structure it is controlled by the processing conditions. Low and medium density resins are prepared by the high pressure processes utilizing air or peroxide catalysts and are characterized by the presence of alkyl side branches. High density resins are prepared in the presence of metals or metallo-organic catalysts at low pressures and are characterized by a reduced number of side branches and an increase in either terminal (vinyl) unsaturation or internal transolefinic structures.

DENSITY <sup>49</sup>

**Scope**—This method is intended for the determination of the density of polyethylene in the range of 0.91 to 0.97.

**Principle**—This method is based on the observation of the level to which a sample sinks in a liquid column exhibiting a density gradient, in comparison with standards of known density.

**Apparatus** Density Gradient Tube—A 1000 ml graduated cylinder equipped with a rubber stopper is suitable.

**Constant Temperature Bath**—The bath should operate at a temperature of  $23^\circ \pm 0.1^\circ\text{C}$ .

**Glass Floats**—Prepare a number of spherical glass floats from Pyrex tubing of various diameters. The maximum diameter of the spheres should be 5 mm. Calibrate the floats as prescribed below.

**Pycnometer**

**Apparatus for Gradient Tube Preparation**—See Fig. 41.24

**Reagents** Isopropanol

Diethylene Glycol

Dewater the liquids prior to use by gently heating or applying vacuum.

**Calibration of Floats**—Place a 1000-ml cylinder in the  $23^\circ \pm 0.1^\circ\text{C}$  constant temperature bath. Fill the cylinder about two-thirds full with a solution of isopropanol and diethylene glycol. The density of the liquid may be varied over the desired range by the addition of either liquid.

When the cylinder and contents have attained temperature equilibrium, place a

<sup>49</sup> ASTM Standards Pt. 9 D1505-57T ASTM Philadelphia, 511, 1957

float in the solution. If the float sinks, add diethylene glycol with good stirring until the float remains stationary for 30 min. If the float rises, add isopropanol with good stirring until the float remains stationary for 30 min. During these periods the cylinder should be covered. After a suitable liquid mixture has been prepared, determine the density of the liquid at  $23^{\circ} \pm 0.1^{\circ}\text{C}.$ , using a pycnometer. Make suitable "in vacuo" corrections for all weighings. Record the density as the density of the float.

Calibrate a series of glass floats covering the density range of 0.91 to 0.97. If necessary to obtain a suitable range of floats, grind the floats to the desired density by rubbing the bead part of the float on a glass plate on which is spread a thin slurry of 400- or 600-mesh silicon carbide.

**Preparation of Gradient Tube.**—Assemble the apparatus as shown in Fig. 41-24. Add 610 ml. of isopropanol and 740 ml. of diethylene glycol to beaker *B*. Stir the solution with a high-speed, propeller-type stirrer or a magnetic stirrer, at such a speed that the surface of the liquid does not fluctuate greatly.

Place 1500 ml. of isopropanol in beaker *A*. Prime the siphon tubes with their respective liquids. Partially open the stopcock on the siphon tube connecting beaker *B* to the gradient tube. Adjust the rate of flow so that at least 60 min. is required to fill the tube. Fill the tube to the 1000-ml. mark.

**Calibration of Gradient Tube.**—Dip at least 7 clean calibrated floats, covering the effective range of the column, into isopropanol, and add them to the tube. Mix the different layers of the tube by stirring horizontally until the floats span the entire range of the gradient tube. A vertical distance of 1 mm. should represent density differences no greater than 0.001 g. per milliliter. If the floats do not spread out evenly in the tube, discard the liquid and prepare a fresh gradient solution. When the desired range is obtained, cap the tube and keep it in the constant temperature bath for 24 hr. prior to use.

Prepare a plot of the density of the floats versus the heights of the floats. The curve should be fairly smooth and nearly linear. If an irregular curve is obtained, the entire procedure should be repeated.

**Procedure.**—Condition the sample for 1 hr. at  $100^{\circ}\text{C}.$  in water or steam, if Type I or II, and at  $120^{\circ}\text{C}.$  if Type III. Cool the sample in a closed vessel for at least 1 hr.

Wet a conditioned sample with isopropanol and gently place it into the gradient tube containing the glass floats. Allow a minimum of 10 min. for the tube and sample to reach equilibrium. Films of 1 to 2 ml. thickness may require several hours to settle.

Read the height of the floats and the sample by using a line through their center of volume.

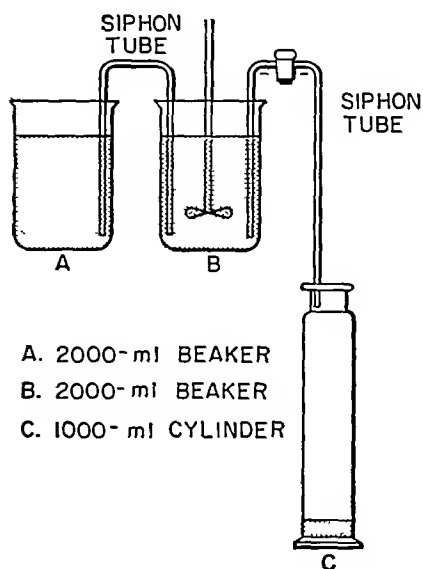


FIG. 41-24. Apparatus for Gradient Tube Preparation.

**Calculations**—Plot the density of the floats versus the heights of the floats. Read the density of the sample from the prepared graph.

**NOTE**—The samples and floats may be removed without destroying the gradient by slowly withdrawing a wire basket attached to a long wire.

### DETERMINATION OF FLOW RATES OF THERMOPLASTICS<sup>50</sup>

**Scope**—This method describes the apparatus and test procedures for measuring the rate of extrusion of a thermoplastic through an orifice under prescribed conditions of temperature and pressure. The flow rate of polyethylene measured according to the conditions of this method is reported as the 'melt index'.

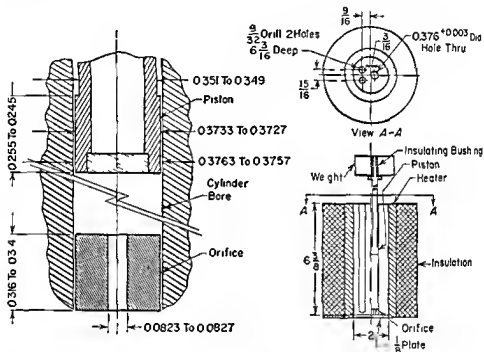


FIG. 41.25 Apparatus for Determining the Flow Rate of Thermoplastics

**Apparatus Extrusion Plastometer.**—See Fig. 41.25. This consists of the following:

**Cylinder**—The cylinder should be a 2 in. diameter steel thermostat  $6\frac{3}{8}$  in. in length with a smooth straight hole  $0.3760 \pm 0.0003$  in. in diameter, displaced  $\frac{3}{16}$  in. from the cylinder axis. Wells for a thermoregulator and thermometer shall be provided as shown in Fig. 41.25. A  $\frac{1}{8}$ -in. plate is attached to the bottom of the cylinder to retain the orifice. A hole in this plate, centered under the orifice and countersunk from below, allows free passage of the extrudate. Two  $\frac{3}{8}$ -in. diameter rods shall be screwed into the side of the cylinder for attaching to a vertical support. The essential dimensions of a satisfactory cylinder of this type are shown in Fig. 41.25.

<sup>50</sup> ASTM Standards, Pt. 9, D1238-57T, ASTM, Philadelphia, 398, 1957.

*Orifice.*—The outside of the orifice cylinder should be such that it will fall freely to the bottom of the 0.376-in. diameter hole in the cylinder. The orifice should have a smooth straight bore  $0.0825 \pm 0.0002$  in. in diameter, and should be  $0.315 \pm 0.001$  in. in length.

*Piston.*—The piston should be made of steel with an insulating bushing at the top as a barrier to heat transfer from the piston to the weight. The land of the piston should be  $0.3730 \pm 0.0003$  in. in diameter and  $0.250 \pm 0.005$  in. in length. Above the land the piston should be relieved to about 0.350 in. in diameter. The combined weight of piston and load should be 2160 g.  $\pm 0.5\%$

*Cylinder Heater.*—The cylinder may be heated with two 100-watt electric band heaters covering the entire length of the cylinder (suitable heaters may be purchased from Industrial Heater Co., 245 Canal Street, New York, N. Y., Catalog No. X-20994-3). After installation of the heaters, the apparatus should be lagged with  $1\frac{1}{2}$  in. of foamed glass insulation. Adjust the heaters to maintain the temperature of the cylinder at  $190^\circ \pm 0.2^\circ\text{C}$ .

*Thermoregulator.*—A mercury thermoregulator having an angle form with a  $2\frac{3}{4}$ -in. body,  $6\frac{1}{10}$ -in. stem to inside of bend,  $1\frac{1}{8}$ -in. bulb, and a bulb diameter of not over  $\frac{1}{4}$  in. may be used to regulate the temperature.

*Thermometer.*—The thermometer should have the same dimensions as the regulator with a range of  $4^\circ\text{C}$ ., graduated in  $0.2^\circ\text{C}$ . divisions.

*Procedure.*—Bring the cylinder and piston to the test temperature of  $190^\circ\text{C}$ . After the apparatus has been at the test temperature for at least 15 min., remove the piston and charge the cylinder with the amount of sample shown below for the anticipated flow rate.

<i>Flow Rate, Grams per 10 Min.</i>	<i>Weight of Sample, Grams</i>	<i>Time Interval, Minutes</i>
0.15 to 1.0	3 to 4	6
1.0 to 3.5	4 to 5	3
3.5 to 10	6 to 8	2
10 to 25	6 to 8	1

As soon as the sample is charged to the cylinder, place a loaded piston weighing 2160 g. in position, and start the timer. After 5 min., cut off the extruded portion flush with the orifice and discard. If a flow rate of 10 g. or greater per 10 min. is being measured, the loss of sample during this preheat period may be excessive. If such is the case, a smaller weight may be used on the piston during this preheat period. At the end of the 5-min. preheat period, replace the smaller weight with the 2160 g. weight. The 5-min. cutoff is then made after changing weights.

After another 1 min., cut off and discard the extruded portion. Then collect the extruded portion according to the time given above. Weigh the extrudate to the nearest milligram. If it contains visible air bubbles, discard the complete charge and repeat the test.

Discharge the remainder of the sample and push the orifice out through the top of the cylinder. Clean the orifice and cylinder immediately.

*Calculation.*—The melt index is reported as the rate of extrusion in grams per 10 min.

**Preparation of Standard Curve.**—Weigh 100 mg. of 2,6-di-*tert*-butyl-*p*-cresol (DTBC) into a 500-ml. volumetric flask. Dissolve in isooctane and dilute to volume with the same solvent. Pipet 0-, 1-, 3-, and 5-ml. aliquots of the solution into 25-ml. volumetric flasks, and dilute to volume with isooctane. Measure the absorbances of the solutions in a 1-cm. cell at 285  $m\mu$ . Use a blank containing only isooctane as the reference solution. Plot the absorbance data against the number of micrograms of DTBC.

**Procedure.**—Weigh 5 g. of the finely divided sample into a 2-oz., wide-mouthed bottle. Add 25.0 ml. of isooctane. Place a piece of aluminum foil over the mouth of the bottle and screw the cap on tightly. Place the bottle on a mechanical shaker and shake for 48 hr. Filter the solution into a 50-ml. beaker. Transfer a portion of the filtrate to a 1-cm. cell, and measure the absorbance at 285  $m\mu$ . Use a blank containing only isooctane as the reference solution.

**Calculation.**—From the calibration curve, read the number of micrograms of 2,6-di-*tert*-butyl-*p*-cresol.

$$2,6\text{-di-}tert\text{-butyl-}p\text{-cresol, p. p. m.} = \frac{\text{micrograms of DTBC}}{\text{weight of sample, grams}}$$

### CARBON BLACK<sup>53</sup>

**Apparatus.** Electric Furnace.—The furnace must be at least 8 in. long, and suitable for use with 1½-in. diameter tubing.

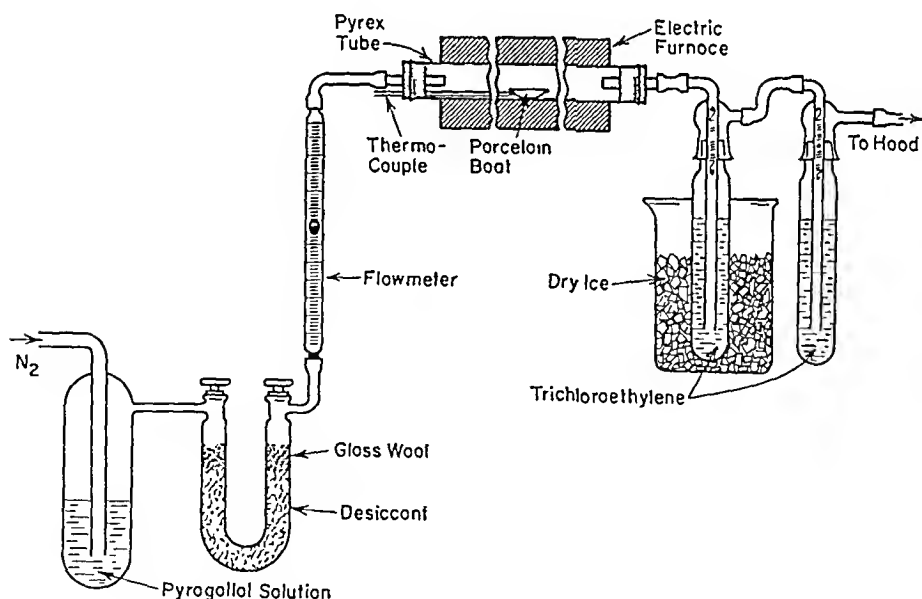


FIG. 41-26. Apparatus for Determining Carbon Black in Plastics.

**Tubing.**—Pyrex or Vycor, 1½-in. diameter, and approximately 4 in. longer than the furnace.

<sup>53</sup> ASTM Standards, Pt. 9, D1603-58T, ASTM, Philadelphia, 508, 1958.

liquid in the reservoir into the upper bulb by using a rubber bulb attached to the left hand tube.

Remove the cap on the right hand tube as soon as the liquid is about 0.5 in.

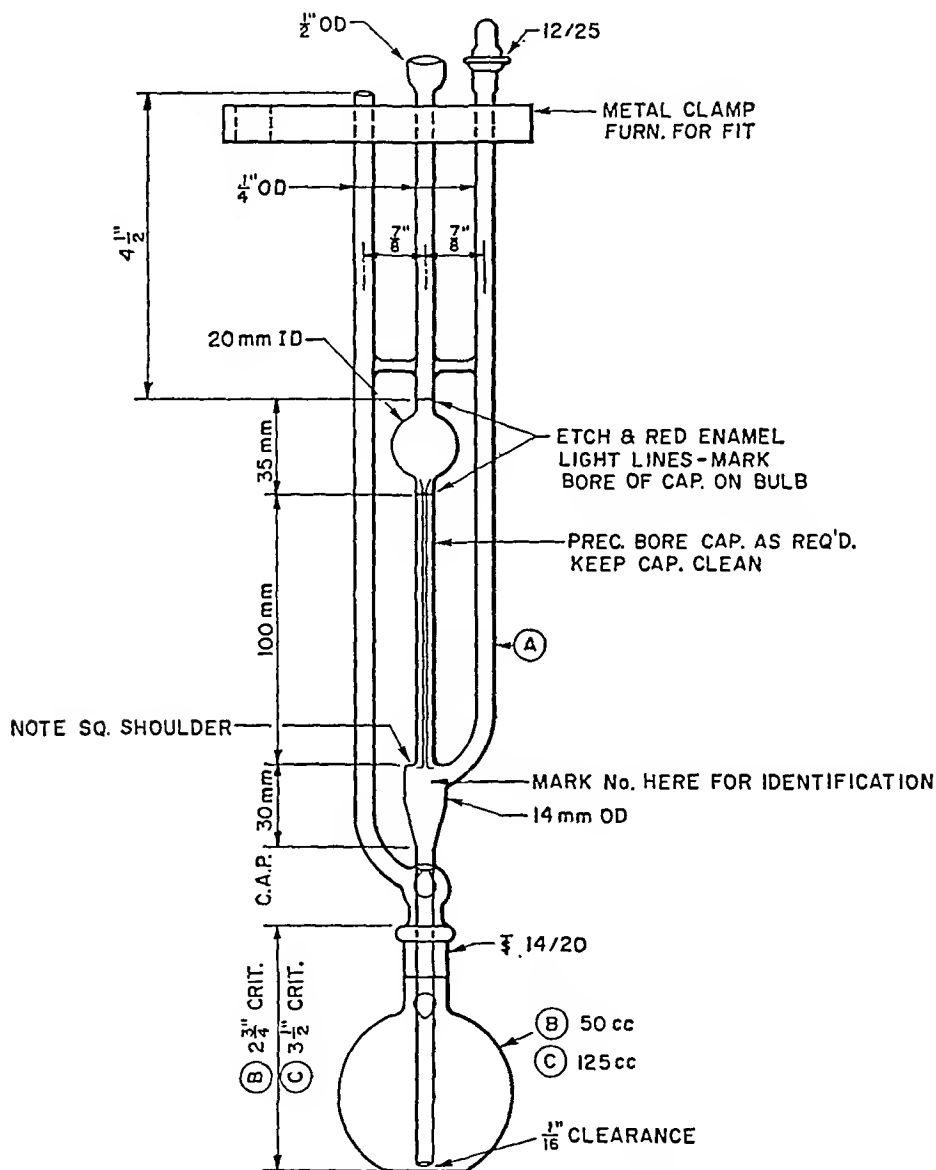


FIG. 41-27. Modified Ubbelöhde Viscosimeter.

above the top calibration mark. Measure the time required for the liquid meniscus to flow between the 2 calibration marks. Duplicate flow-time measurements should agree within 0.2 sec. Determine the solvent flow time similarly.

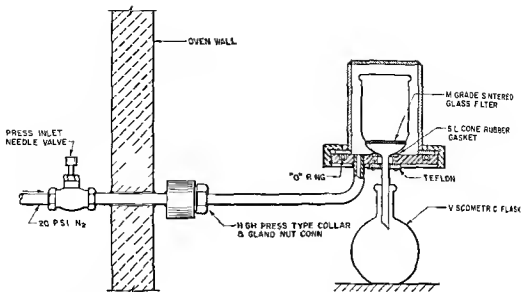


FIG. 41-28 Apparatus for Filtration of Polyethylene Solutions at Elevated Temperatures

#### Calculation -

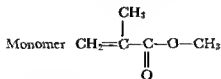
$$\text{Concentration } (c) \text{ in grams per 100 ml} = \frac{\text{weight of sample} \times 0.881}{\text{weight of solvent}} \times 100$$

$$\text{Inherent viscosity} = \frac{2.303}{c} \log_{10} \frac{\text{flow time of solution}}{\text{flow time of solvent}}$$

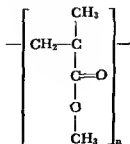
### ACRYLIC PLASTICS

Acrylic plastics are based on resins made by the polymerization or copolymerization of acrylic monomers such as ethyl acrylate and methyl methacrylate

#### POLYMETHYL METHACRYLATE



Polymer structure



METHYL METHACRYLATE MONOMER <sup>55</sup>

*Scope.*—The following polarographic procedure is suitable for the determination of total acrylic monomers in plastics. It will not differentiate between monomers such as methyl methacrylate and ethyl acrylate.

*Apparatus.* Polarograph, Recording.—Leeds and Northrup Electro-Chemograph Type E, or equivalent.

*Polarographic Cell.*—Equipped with a saturated calomel electrode connected through a bridge containing 0.1 *N* tetra-*n*-butyl ammonium hydroxide. The cell system must be protected from the air.

*Reagents.* Benzene, c.p.

Ethanol, 2B Absolute.

Methyl Methacrylate Monomer.—Use the best material available.

*Calibration.*—Place 20 to 30 ml. of benzene in a 100-ml. volumetric flask and weigh. Add about 100 mg. of the monomer to the flask, stopper, and reweigh. Dilute to volume with the same solvent.

Weigh 1 g. of the reprecipitated or monomer-free plastic into each of five 50-ml. volumetric flasks. Add 40 ml. of benzene, and shake until the plastic is dissolved. Pipet into 4 of the flasks, aliquots of the monomer solution ranging from 1 ml. to 10 ml. (equivalent to 0.1 to 1% monomer in the plastic). Reserve the fifth flask as the blank. Dilute the solutions to volume with benzene. Transfer a 5-ml. aliquot of each of the prepared standards to a 10-ml. volumetric flask. Add 1 ml. of polarographic grade 1 *M* tetra-*n*-butyl ammonium hydroxide to each flask, and dilute to volume with ethanol.

Transfer a portion of the solution to the polarographic cell, and flush briefly with hydrogen gas. Overblowing will result in loss of sample. Obtain the polarogram as soon as most of the oxygen is removed. If the cell is connected during this short blowing process, the extent of the oxygen removal can be followed by observation of the indicator needle, which will return nearly to the base line. Start recording when the needle reaches a few divisions from the starting point. Set the current range for 5  $\mu$ a. for full scale and record from  $-1.4$  to  $-2.4$  v. The half-wave potential for acrylic monomers is approximately  $-1.85$  v.

Using the method of tangents, measure the diffusion current for each sample, and plot this current expressed in scale divisions versus concentration of acrylic monomer in milligrams.

*Procedure.*—Weigh 1 g. of plastic into a 50-ml. volumetric flask, and dissolve in benzene. Dilute to volume and, after mixing, transfer a 5-ml. aliquot to a 10-ml. volumetric flask. Add 1 ml. of 1 *M* tetra-*n*-butyl ammonium hydroxide, and dilute to volume with ethanol. Obtain the polarogram of a portion of the solution as described in the third paragraph of the "Calibration," above.

*Calculations.*—Measure the diffusion current and record the corresponding number of milligrams of monomer from the calibration curve.

$$\text{Methyl methacrylate monomer, per cent} = \frac{\text{milligrams of monomer}}{\text{milligrams of sample in aliquot}} \times 100$$

LAURYL MERCAPTAN <sup>56</sup>

*Principle.*—The mercaptan is titrated amperometrically with silver nitrate in ammoniacal medium. A platinum electrode is placed in the solution to be titrated

<sup>55</sup> Lacoste, R. J., Rosenthal, I., and Schmettinger, C. H., *Anal. Chem.*, 28, 983, 1956.

<sup>56</sup> Daniels, O. L., The Dow Chemical Co., unpublished data.



and in electrolytic connection is made through a salt bridge to a reference electrode. Any current produced is measured on a microammeter. No current flows until an excess of silver ion is present at the end point. No external e.m.f. need be applied.

**Apparatus** Mercury-Mercuric Iodide Half Cell—Connected through a salt bridge containing approximately 0.1 M ammonium nitrate to a platinum electrode.

Microammeter—Range 0 to 50  $\mu$ A

Titration Cell—Use a 150 ml beaker with magnetic stirrer.

Buret, 10 ml

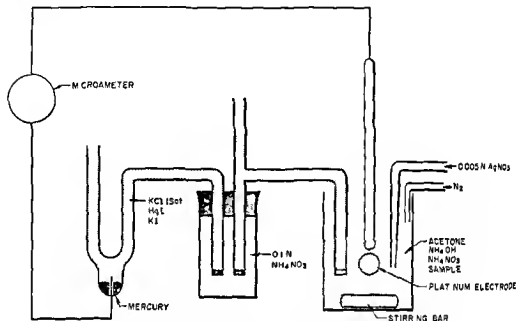


Fig. 41-29 Apparatus for Titration of Mercaptans

**Reagents** Electrolyte Solution—Dissolve 4.2 g of potassium iodide and 1.3 g of mercuric iodide in 100 ml of saturated potassium chloride solution.

Silver Nitrate, 0.005 N—Dissolve 0.8495 g of reagent grade silver nitrate in water; dilute the solution to 1 liter in a volumetric flask and mix well.

Acetone—Free from interfering substances.

**Procedure**—Assemble the apparatus (Fig. 41-29) so that the mercury-mercuric iodide half cell is electrolytically connected through a salt bridge containing ammonium nitrate to a second half cell containing a platinum electrode. These 2 half cells are connected through a microammeter.

Weigh 2 g of the plastic into a 150 ml beaker and add 100 ml of acetone. Stir the mixture to facilitate dissolution of the plastic. Add 5 ml of 5 M ammonium hydroxide and 5 ml of 1 M ammonium nitrate solution. Continue stirring until the plastic redissolves.

Immerse the tip of the ammonium nitrate bridge, the platinum electrode, and the tip of a buret into the solution. Titrate by slowly adding 0.005 N silver nitrate until a current begins to flow. Continue the titration using small increments until the diffusion current of the excess silver shows that the end point is passed.

**Calculations.**—Plot the readings of the microammeter against the volume of silver nitrate added. The point of intersection of 2 lines drawn through the plotted points will correspond to the end point. The current before the end point (residual current of the medium) is practically zero.

$$\text{Lauryl mercaptan, per cent} = \frac{\text{milliliters of AgNO}_3 \times N \times 0.202}{\text{grams of sample}} \times 100$$

#### BENZOYL PEROXIDE <sup>57</sup>

**Principle.**—The sample is dissolved in methylene chloride, and a blue color is developed by addition of phenothiazine. The color is stable and may be measured on an ordinary spectrophotometer.

**Apparatus.** Spectrophotometer.—Beckman DU or equivalent.

**Optical Cells.**—Corex, 10-mm. light path.

**Reagents.** Methylene Chloride, Technical.

**Phenothiazine Solution.**—Dissolve 100 mg. of recrystallized phenothiazine in 100 ml. of methylene chloride.

**Benzoyl Peroxide Standard Solution, 100  $\mu$ g. per ml.**—Dissolve 10 mg. of benzoyl peroxide in methylene chloride, and dilute to 100 ml. with methylene chloride in a volumetric flask.

**Preparation of Calibration Curve.**—Pipet aliquots of the standard solution containing from 100 to 1000  $\mu$ g. of benzoyl peroxide into respective 25-ml. volumetric flasks. Add methylene chloride to give a total volume of 20 ml., and mix. Add 1 ml. of the phenothiazine reagent, and make to volume with methylene chloride. Mix each solution thoroughly, allow to stand 5 min., and measure the absorbance in a 10-mm. cell at 618  $m\mu$ . Use a blank containing only methylene chloride and phenothiazine as the reference solution. Plot the absorbance data against the number of micrograms of benzoyl peroxide.

**Procedure.**—Weigh 0.2 g. of the finely subdivided sample into a 25-ml. volumetric flask containing about 20 ml. of methylene chloride. Dissolve the sample and add 1 ml. of the phenothiazine reagent. Make the solution to volume with methylene chloride and mix. Allow it to stand 5 min. Filter the solution, if necessary, and determine the absorbance at 618  $m\mu$  in a 10-mm. cell, using a blank of methylene chloride and phenothiazine as the reference solution.

**Calculation.**—From the calibration curve, read the number of micrograms of benzoyl peroxide present.

$$\text{Benzoyl peroxide, p. p. m.} = \frac{\text{micrograms of benzoyl peroxide}}{\text{grams of sample}}$$

#### METHYL SALICYLATE <sup>58</sup>

**Principle.**—The sample is dissolved in chloroform. Methyl salicylate is extracted with sodium hydroxide, and determined through its ultraviolet absorption at 302  $m\mu$  in dilute hydrochloric acid.

**Apparatus.** Ultraviolet Spectrophotometer.—Beckman Model DU or equivalent.

**Calibration.**—Weigh 0.1000 g. of pure methyl salicylate, and dilute to 250 ml. with  $\text{CHCl}_3$  in a volumetric flask. Weigh  $1.0 \pm 0.1$  g. of reprecipitated or additive-

<sup>57</sup> Daniels, O. L., The Dow Chemical Co., unpublished data.

<sup>58</sup> Cummert, W. B., The Dow Chemical Co., unpublished data.

free plastic in a 100 ml beaker. Add approximately 2 ml of  $\text{CHCl}_3$  and allow the mixture to stand a few minutes then add 23 ml more of  $\text{CHCl}_3$ . Pipet in 250 ml of the methyl salicylate standard solution. Prepare also a blank containing only the reprecipitated plastic in 50 ml of  $\text{CHCl}_3$ .

Cover each beaker with a watch glass and allow the mixtures to stand until the plastic is completely dissolved. Transfer each chloroform solution to a 125 ml separatory funnel and extract it with three 50.0 ml portions of 2% sodium hydroxide. Filter the aqueous extracts through a medium 12.5-cm folded filter paper (Reeve Angel No. 871) which has been moistened with water. Collect the filtrate in a 250 ml volumetric flask containing 6.7 ml of 36% hydrochloric acid. Wash the paper with distilled water. Dilute the filtrate and washings to the mark and mix thoroughly. Transfer a portion of the final solution to a 1.0 cm cell and read the absorbancy at 302  $m\mu$  using a slit width of 0.4 mm. Water serves as the reference liquid. Correct for the blank if necessary.

Divide the weight of the methyl salicylate present (in 250 ml of the final solution) by the absorbancy reading to obtain a coefficient  $C$ . This should have a value of about 0.0103 g per 250 ml per absorbancy unit.

**Procedure**—Weigh a 1.0 g sample to the nearest milligram in a small beaker and add 2 ml of chloroform. Allow the beaker and contents to stand a few minutes and add 48 ml more of chloroform. Prepare a blank also and proceed as in the second paragraph of Calibration above the blank may be omitted if the reagents used do not show ultraviolet absorption at 302  $m\mu$ .

**Calculation**—Let  $A$  equal the absorbancy reading on the final solution of the sample and let  $S$  be the number of grams of sample represented in 250 ml of the same solution

$$\text{Methyl salicylate per cent} = \frac{A \times C \times 100}{S}$$

### VINYL ACIDS<sup>59</sup>

**Principle**—The plastic is dissolved in chloroform and the acid groups are titrated with alcoholic sodium hydroxide using thymol blue as indicator. Any free acids will be included.

**Reagents** Chloroform—Technical grade free from color and acid impurities.

Methanol—Redistilled or reagent grade.

**Sodium Hydroxide in Methanol** Approximately 0.1  $N$ —Dissolve 4.0 g of reagent grade sodium hydroxide in 10 ml of water and dilute the solution to 1 liter with methanol.

**Hydrochloric Acid 0.1  $N$  Standard Solution**—Standardize by any convenient and reliable method.

**Thymol Blue Indicator Solution**—Dissolve 0.3 g of thymol blue in 100 ml of methanol.

**Procedure**—Weigh a 0.5 g sample of the plastic into a 250 ml Erlenmeyer flask. Add 2 ml of chloroform and let stand a minute so that the pieces of plastic will adhere to the bottom of the flask. Add 50 ml of chloroform cover the flask with a small watch glass and swirl occasionally until the sample has dissolved. If the solution becomes cloudy because the sample is not completely soluble in chloroform add a few milliliters of methanol. Add 0.1 ml of thymol blue indicator.

solution and titrate with 0.1 *N* methanolic-sodium hydroxide. The color change at the end point is from yellow or brownish-yellow to blue or violet.

Titrate a solvent blank in the same way. Correct the titration in the above paragraph for the volume of 0.1 *N* sodium hydroxide consumed by the blank.

Standardize the 0.1 *N* sodium hydroxide solution at the time of use by the following procedure: pipet 20 ml. of standard 0.1 *N* hydrochloric acid into an Erlenmeyer flask; add 0.1 ml. of thymol blue indicator solution, and titrate to a blue or violet end point with the 0.1 *N* sodium hydroxide; calculate the true normality of the sodium hydroxide solution.

Calculations.—

$$\text{Acrylic acid, per cent} = \frac{\text{net milliliters of NaOH} \times N \times 0.0721}{\text{sample weight in grams}} \times 100$$

$$\text{Methacrylic acid, per cent} = \frac{\text{net milliliters of NaOH} \times N \times 0.0861}{\text{sample weight in grams}} \times 100$$

## ACRYLIC COPOLYMERS

### DETERMINATION OF TOTAL METHYL, ETHYL, AND/OR BUTYL ESTERS IN ACRYLIC COPOLYMERS<sup>60</sup>

*Scope.*—This procedure is suitable for determining the amounts of the various acrylic acid and methacrylic acid esters in copolymers. It will not, however, distinguish between acrylate and methacrylate esters of the same alcohol.

*Principle.*—The method consists of 2 separate determinations. First, the total alkoxyl is determined by a modified Zeisel procedure. Secondly, the various alkoxyl groups, after being converted to the corresponding alkyl iodides, are separated and measured by gas chromatography.

*Apparatus.* Distillation Unit for the Alkoxyl Determination.—(See Fig. 41-30.)

Distillation Unit for the Alkyl Iodide Absorption.—(See Fig. 41-31.)

*Gas Chromatograph.*—See "Apparatus," p. 2041. The column is a 9-ft. length of ¼-in. stainless steel tubing, packed with 20% di-2-ethylhexyl sebacate on firebrick (42 to 60 mesh). It is operated at a temperature of 70°C. and a helium pressure of 8 lbs. p.s.i. (flow rate of 52 ml. per minute).

*Reagents.* Potassium Acetate Solution.—Dissolve 100 g. of potassium acetate in 1 liter of a solution containing 900 ml. of glacial acetic acid and 100 ml. of acetic anhydride.

Bromine Solution.—Dissolve 5 ml. of bromine in 145 ml. of the potassium acetate solution. Prepare fresh daily.

Sodium Acetate Solution.—Dissolve 220 g. of sodium acetate in water and dilute to 1 liter.

Dilute Sulfuric Acid.—Carefully mix 1 volume of reagent grade sulfuric acid with 9 volumes of water.

Hydriodic Acid, 57%.—Hydriodic acid forms with water a constant-boiling mixture (boiling point 126° to 127°C.), which contains 57% HI. The concentration of HI in the reagent used should be not less than 56.5%. If necessary, the acid may be purified by adding to it a small amount of red phosphorus and boiling for

<sup>60</sup> Haslam, J., Hamilton, J. B., and Jeffs, A. R., *Analyst*, 83, 66, 1958; Samsel, E. P., Miller, D. L., and Cobler, J. G., paper presented at the Regional Meeting of The American Chemical Society, Detroit, 1960.

20 to 30 min in a hood, while passing a stream of  $\text{CO}_2$  into the liquid. Distillation is then carried out behind a safety glass shield in a hood, using an all glass apparatus with a slow stream of  $\text{CO}_2$  running through the receiver. *Caution*—The distillation

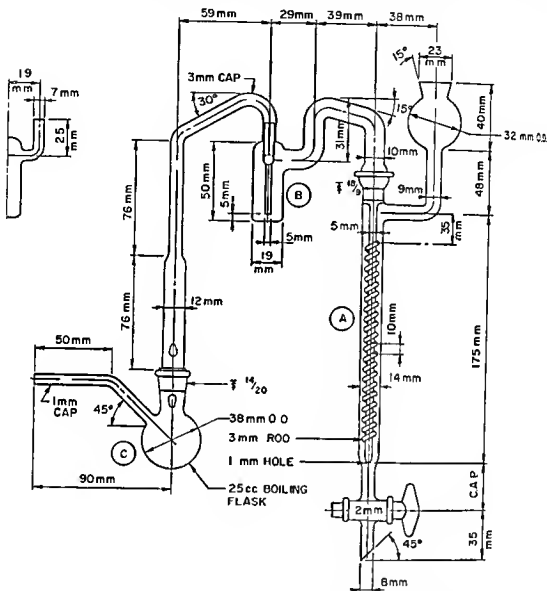


FIG 41 30 Distillation Unit for Alkoxy Determination

should not be carried too far, since the phosphorus reaction product sometimes explodes near the end. Keep the current of  $\text{CO}_2$  going after the distillation is ended and until the apparatus has cooled. Place the purified HI in small brown glass stoppered bottles, previously swept out with  $\text{CO}_2$ , and seal with molten paraffin.

**Procedure 1 Determination of Total Alkoxy**—Add 3 ml of water to the scrubbing trap, and 10 ml of bromine acetic acid solution to receiver A (Fig 41 30)

Attach the receiver to the distillation apparatus, B. Weigh a 50-mg. sample into the side-arm flask, C, add 3 cc. of melted phenol, and warm on a steam bath until the sample is dissolved. Occasionally it is necessary to add a small amount of

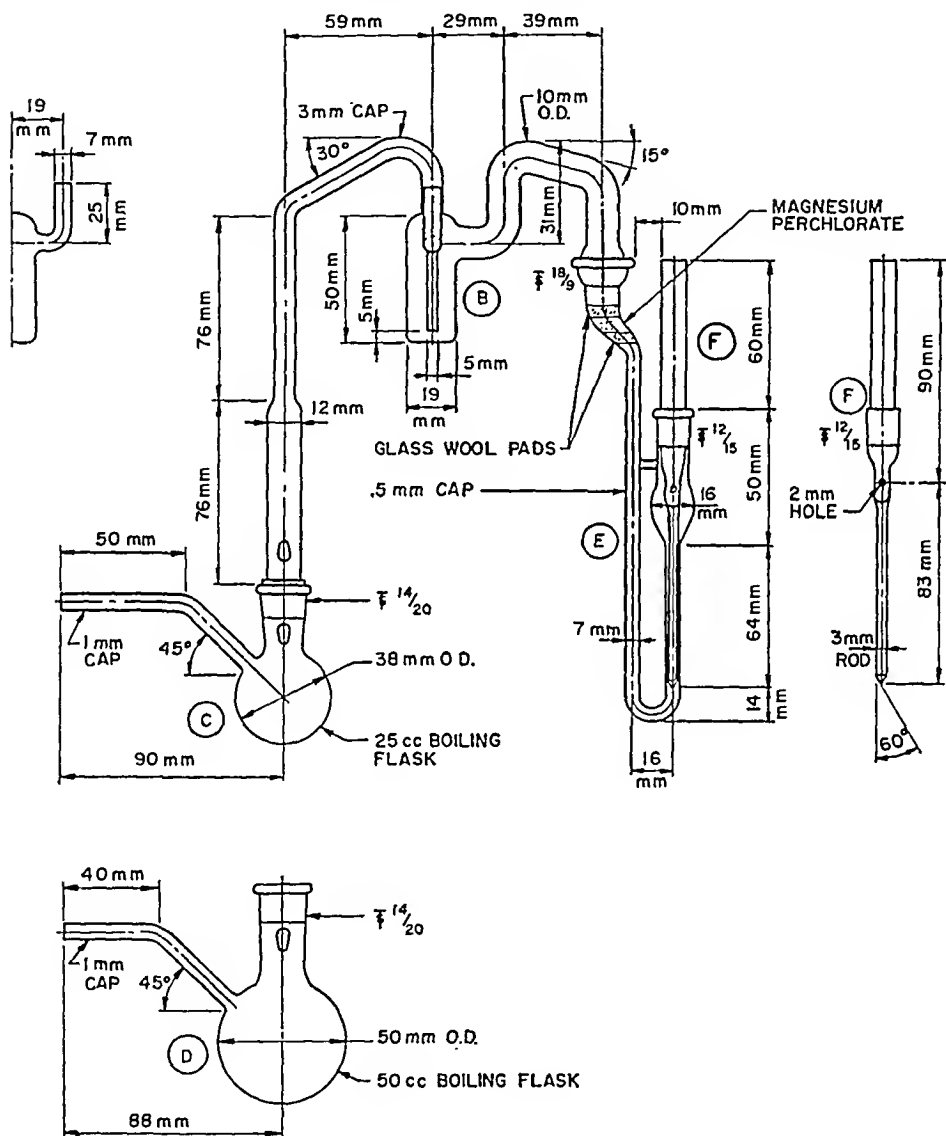


FIG. 41-31. Distillation Unit for Alkyl Iodide Absorption.

propionic anhydride to the phenol mixture, with further warming, to achieve solution. Add 6 cc. of constant boiling hydriodic acid to the flask, and attach at once to the apparatus as shown. With some types of polymers, the addition of hydriodic acid will precipitate the sample. If this occurs, gently shake the reaction flask from time to time so that the precipitate floats free in the boiling mixture. Connect

the side arm to a source of nitrogen and pass a current of the gas into the apparatus at a rate of 2 bubbles per sec. Immerse the flask in an oil bath maintained at 150°C and heat for 3 hr.

Wash the contents of the receiver into a flask containing 15 ml of sodium acetate solution. Add formic acid dropwise to reduce the bromine and then add about 6 drops more. A total of 10 to 12 drops is usually required. Add 3 g of potassium iodide and 15 ml of dilute sulfuric acid. Titrate the liberated iodine with 0.1 N sodium thiosulfate. Make a blank determination.

**Procedure 2 Separation of Alkyl Iodides**—The hydriodic acid hydrolysis of the polymeric sample is carried out in exactly the same manner as before except that an absorber tube is substituted for the bromine receiver. The details of the tube are shown in Fig. 41.31. Place a small amount of drying agent (magnesium perchlorate) into the inlet section of the absorber tube. With a hypodermic syringe add 0.25 cc of *n*-heptane to the outlet section and assemble the apparatus as shown. Surround the tube with a dry ice bath at -80°C and allow the reaction to proceed at 150°C for 90 min.

At completion of the hydrolysis disconnect the trap and allow it to warm to room temperature. By means of a microsyringe inject a small amount of the heptane solution into the gas chromatograph system.

**Calculations**—Measure the individual peak areas and compute the total area

$$V_{me} = \frac{A_{me}}{A_{me} + A_{et} + A_{bu}} \times V_t$$

$$V_{et} = \frac{A_{et}}{A_{me} + A_{et} + A_{bu}} \times V_t$$

$$V_{bu} = \frac{A_{bu}}{A_{me} + A_{et} + A_{bu}} \times V_t$$

$$\text{Methyl methacrylate, per cent} = \frac{V_{me} \times 0.1668}{\text{sample weight}}$$

$$\text{Ethyl acrylate, per cent} = \frac{V_{et} \times 0.1668}{\text{sample weight}}$$

$$\text{Butyl acrylate, per cent} = \frac{V_{bu} \times 0.2133}{\text{sample weight}}$$

where  $V_t$  = volume of 0.1 N  $\text{Na}_2\text{S}_2\text{O}_3$  required for total alkoxyl

$A_{me}$  = area under methyl iodide peak,

$A_{et}$  = area under ethyl iodide peak

$A_{bu}$  = area under butyl iodide peak,

$V_{me}$  = volume of 0.1 N  $\text{Na}_2\text{S}_2\text{O}_3$  required to titrate  $\text{CH}_3\text{I}$ ,

$V_{et}$  = volume of 0.1 N  $\text{Na}_2\text{S}_2\text{O}_3$  required to titrate  $\text{C}_2\text{H}_5\text{I}$  and

$V_{bu}$  = volume of 0.1 N  $\text{Na}_2\text{S}_2\text{O}_3$  required to titrate  $\text{C}_4\text{H}_9\text{I}$

Greater accuracy in the analysis of 2 component systems may be attained through the use of a calibration curve. The calibration curve is prepared by carrying known mixtures through the hydrolysis gas chromatographic procedure and plotting the recovery versus the amount added. Alternatively, the calculations may be

based on the peak areas produced by known amounts of the alkyl iodides without resorting to the total alkoxy-ratio procedure.

#### TOTAL LONG CHAIN ALCOHOL ESTERS<sup>61</sup>

**Scope.**—This procedure is suitable for determining acrylic acid esters such as 2-ethylhexyl, decyl, and lauryl acrylate in copolymers. The procedure measures the sum of the monomeric and polymerized esters.

**Principle.**—The copolymer is dissolved in tetrahydrofuran and saponified with alcoholic KOH. The saponification mixture is acidified, and an aliquot is injected into a gas chromatography apparatus. The peak area produced by the alcohol formed during the saponification is compared with the area produced from known amounts of the monomeric acrylic acid ester carried through the same procedure.

**Apparatus.** Gas Chromatograph.—Beckman GC-2A or equivalent, with hydrogen flame detector.

**Column.**—The column consists of  $\frac{1}{4}$  in. I.D. stainless steel tubing, 4-ft. length, packed with 23% Oronite NI-W Dispersant on firebrick (42 to 60 mesh).

**Microsyringe,** 0.0 to 10.0  $\mu$ l.

**Parr Bomb,** 22-ml.—Stainless steel, with lead gasket.

**Oven.**—Operating at 160°C., and equipped with a device for slowly rotating the bombs.

**Bottles,** 1-oz.—French square.

**Reagents.** Compressed Gases.—See following section, on operating conditions.

**Ethanol.**—Formula 2B absolute.

**Tetrahydrofuran.**

**Alcoholic Potassium Hydroxide.**—Dissolve 15 g. of reagent grade KOH in 50 ml. of formula 2B absolute ethanol.

**Acrylate Monomer.**—Commercial grade.

**Operating Conditions for Gas Chromatograph.**—(a) Helium gas pressure, 30 to 40 p.s.i. (100 to 150 ml. per min.); (b) compressed air pressure, 16 p.s.i.; (c) hydrogen gas pressure, 7 p.s.i.; (d) column temperature, 160°C.; (e) attenuator,  $5 \times 10^2$ ; (f) recorder, 0 to 1 mv.

**Standardization.**—Accurately weigh 25 to 50 mg. of the desired acrylate monomer into the Parr bomb. Add 13 ml. of tetrahydrofuran and 3 ml. of alcoholic KOH solution.

Assemble the bomb, making sure the head gasket is in place, and tighten with a wrench. Place the bomb in the rotating device in the oven and rotate slowly at 16°C. for 4 hr. Remove the bomb from the oven, and allow it to cool to room temperature. Remove the lid and transfer the contents of the bomb to a 25-ml. volumetric flask. Rinse the bomb and bomb lid with formula 2B absolute ethanol, and add the rinsings to the flask. Dilute to volume with the ethanol.

Transfer a 10-ml. aliquot of the solution to a 1-oz. French square bottle and add, by pipet, 0.50 ml. of concentrated HCl. Cap the bottle and shake for several seconds. Allow the precipitate to settle. By means of a micro-syringe, inject 3  $\mu$ l. of the supernatant liquid into the gas chromatographic apparatus.

Measure the area of the resulting alcohol peak.

**Procedure.**—Accurately weigh 400 to 500 mg. of the copolymer into a Parr bomb. Dissolve the sample in 13 ml. of tetrahydrofuran. Add 3 ml. of the alcoholic KOH solution, and proceed as directed in the second and third paragraphs, above.

<sup>61</sup> Cobler, J. G., Miller, D. L., and Samsel, E. P., The Dow Chemical Co., unpublished data.



**Calculations.**—Measure the area of the resulting alcohol peak. Compare the sample peak area with the area produced by the standard monomer solution

$$\text{Acrylic acid ester, per cent} = \frac{A \times B}{C \times D} \times 100$$

where  $A$  = milligrams of monomer in the standard,

$B$  = peak area of sample,

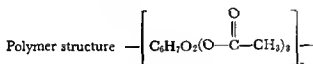
$C$  = peak area of standard, and

$D$  = sample weight in milligrams

## CELLULOSIC PLASTICS

Cellulosic plastics are based on cellulose compounds such as esters (cellulose acetate) and ethers (ethyl cellulose).

### CELLULOSE ACETATE



### PLASTICIZERS<sup>62</sup>

**Solvent.** Ethanol *n* Hexane.—Dilute 1 volume of 2B ethanol with 1 volume of *n* hexane

**Procedure**—Dry the finely subdivided sample at 100°C for 30 min, and cool it in a desiccator. Weigh about 5 g of the dried sample accurately into a Soxhlet thimble. Assemble the Soxhlet extractor, using a tared extraction flask. Extract with the alcohol hexane solvent for 24 hr. Remove the flask and evaporate the solvent nearly to dryness on the steam bath. Transfer the flask and contents to a vacuum desiccator, and dry to constant weight.

**Calculation.**—

$$\text{Plasticizer, per cent} = \frac{B - C}{A} \times 100$$

where  $A$  = weight of the sample before extraction,

$B$  = weight of flask plus residue, and

$C$  = weight of flask

### MOISTURE<sup>63</sup>

**Procedure.**—Weigh accurately about 5 g of the sample into a tared weighing bottle. Place the bottle and contents in an oven for 2 hr at 100° to 105°C. Remove the bottle from the oven, cover, and place it in a desiccator. When cool remove it from the desiccator and reweigh.

**Calculation.**—

$$\text{Moisture, per cent} = \frac{\text{weight of loss on heating}}{\text{weight of sample}} \times 100$$

<sup>62</sup> Whitnack, G. C., and Gantz, E. St. Clair *Anal. Chem.*, **24**, 1060 (1952)

<sup>63</sup> ASTM Standards, Pt. 8, D871-56. ASTM, Philadelphia, 460, 1958

ASH <sup>64</sup>

**Procedure.**—Dry the sample for 2 hr. at 100° to 105°C. Weigh accurately 10 g. of the dried sample into a 100-ml. porcelain crucible, which has been previously ignited and tared. Burn the sample directly over a flame. The sample should burn gently. Continue heating with a burner only as long as the residue burns with a flame. If desired, additional 10-g. portions of the sample may be added when the flame subsides.

Transfer the crucible to a muffle furnace and ignite the carbon at 550° to 600°C. Allow the crucible to cool slightly, and then transfer to a desiccator. When cool, remove the crucible and reweigh.

**Calculation.**—

$$\text{Ash, per cent} = \frac{\text{weight of residue}}{\text{weight of sample}} \times 100$$

FREE ACIDITY <sup>64</sup>

**Procedure.**—Place about 5 g. of sample, accurately weighed, in a 250-ml. Erlenmeyer flask, containing 150 ml. of freshly boiled, cold water. Stopper the flask, shake vigorously, and allow it to stand for 3 hr.

Filter off the cellulose acetate. Wash the residue thoroughly with water. Combine the filtrate and washings, and titrate with 0.01 *N* NaOH to the phenolphthalein end point. Run a blank determination on 150 ml. of water.

**Calculation.**—

$$\text{Free acidity as acetic acid, per cent} = \frac{\text{net milliliters of NaOH} \times N \times .060}{\text{weight of sample}} \times 100$$

COMBINED ACETYL <sup>64</sup>

**Reagents.** Ethanol, 75% by Volume.—Mix 790 ml. of formula 2B or 3A de-natured ethanol with 210 ml. of H<sub>2</sub>O.

**Procedure.**—Grind the sample to pass a No. 20 (840- $\mu$ ) sieve, and dry for 2 hr. at 105°C. Weigh approximately 1 g. of the dried sample to the nearest 0.001 g. and transfer it to a 250-ml. Erlenmeyer flask. Add 40 ml. of the ethanol solution. Loosely stopper the flask, and heat for 30 min. at 50° to 60°C. Add 40 ml. of 0.5 *N* NaOH, and heat again at 50° to 60°C. for 15 min. Stopper the flask tightly, and allow to stand at room temperature for 48 hr. If the acetyl content is over 43%, or if the sample is very hard, allow the flask to stand for 72 hr.

Back-titrate the excess NaOH with 0.5 *N* HCl, using phenolphthalein as the indicator. Add an excess of 1 ml. of 0.5 *N* HCl, and allow the flask to stand overnight. Titrate the excess HCl with 0.5 *N* NaOH until a faint pink end point persists after vigorous shaking of the flask. Carry a reagent blank through the complete procedure.

**Calculation.**—

$$\text{Acetyl. per cent} = \frac{[(A \times N_A) - (B \times N_B)] \times .043}{W} \times 100$$

where *A* = net milliliters of NaOH,

*N<sub>A</sub>* = normality of NaOH,

*B* = net milliliters of HCl,

*N<sub>B</sub>* = normality of HCl, and

*W* = weight of sample.

*Procedure.*—Dry the sample for 1 to 2 hr. at 105°C., and cool in a desiccator. Prepare approximately 340 ml. of a solution of cellulose acetate by adding cellulose acetate and solvent to the bottle in the following proportions.

Ingredients, Percentage by weight	Formula					
	A	B	C	D	E	F
Cellulose acetate, per cent. ....	20	20	20	15	20	10
Acetone, per cent. ....	72	80				
Acetone, { 96 per cent. ....					80	
{ Water, 4 per cent. ....						
Ethanol, per cent. ....	8		8	8.5		
Methanol, per cent. ....						9
Methylene chloride, per cent. ....			72	76.5		81

Formula A, B, or E may be used for cellulose acetate having a maximum acetyl content of 40.5%; formula C should be used for cellulose acetate having an acetyl range of 40.5 to 42.7%, while either formula D or F may be used for cellulose acetate having an acetyl range of 42.7 to 44.8%.

Close the bottle tightly and allow a short time for the solvent to penetrate the sample. Shake the mixture until a uniform solution is obtained. Place the bottle in the constant temperature bath at  $25^{\circ} \pm 0.1^{\circ}\text{C.}$ , and allow the solution to come to temperature.

Open the bottle and drop a  $\frac{3}{32}$ -in. stainless steel ball through the center of the column of solution. Time the fall of the ball between the calibration marks. If the observed time is less than 20 sec. or greater than 100 sec., repeat the measurement using a different ball. If the times of fall for successive measurements vary significantly, use freshly prepared solutions for each measurement.

Determine the density of the solution in grams per milliliter by measuring the volume at  $25^{\circ} \pm 0.1^{\circ}\text{C.}$  of a known weight of the solution in a 100-ml., tightly stoppered, graduated cylinder.

Calculation.—

$$n = K(a - b)t$$

where  $n$  = viscosity in poises,

$K$  = apparatus constant,

$a$  = density of the ball in grams per milliliter,

$b$  = density of the solution in grams per milliliter, and

$t$  = time of fall in seconds.

### ETHYL CELLULOSE

Polymer structure:  $[\text{C}_6\text{H}_7\text{O}_2(\text{OC}_2\text{H}_5)_3]_n$

## PLASTICIZERS

Proceed as prescribed in "Plasticizers, p 2098, above employing a *n* heptane extraction for 8 hr, instead of the ethanol hexane extraction

MOISTURE <sup>67</sup>

The test is carried out in the same way as that for cellulose acetate, p 2098, above

ASH <sup>62</sup>

The test is carried out in the same way as that for cellulose acetate p 2099, above

CHLORIDES <sup>68</sup>

**Procedure**—Dry the sample for 2 hr at 100° to 105°C. Weigh accurately about 10 g of the sample into a 500 ml, wide mouthed Erlenmeyer flask. Add 200 ml of hot water and 10 ml of concentrated HNO<sub>3</sub>. Heat the contents of the flask at the boiling point for 1 to 2 min, and then cool to room temperature. Add 500 ml of 0.1 N AgNO<sub>3</sub> and 5 ml of 5% Fe(NO<sub>3</sub>)<sub>3</sub> solution. Heat the solution on a hot plate to coagulate the precipitated AgCl. Back titrate the excess AgNO<sub>3</sub> with 0.1 N KCNS to the first appearance of a faint pink color.

**Calculation.**—

$$\text{Chlorides, per cent} = \frac{[(A \times N_A) - (B \times N_B)] \times 0.0585}{W} \times 100$$

where *A* = milliliters of AgNO<sub>3</sub> solution,

*N<sub>A</sub>* = normality of AgNO<sub>3</sub> solution,

*B* = milliliters of KCNS solution,

*N<sub>B</sub>* = normality of KCNS solution, and

*W* = weight of sample, in grams

ALKALINITY <sup>69</sup>

**Reagents** Strontium Chloride Solution—Dissolve 100 g SrCl<sub>2</sub> · 6H<sub>2</sub>O in water and dilute to 1 liter

**Procedure.**—Dry the sample for 2 hr at 100° to 105°C. Weigh accurately about 10 g of the sample into a 500 ml Erlenmeyer flask. Add 150 ml of water and heat at the boiling point for 5 min. Add while stirring, 5 ml of SrCl<sub>2</sub> solution. Allow the solution to cool, and titrate with 0.1 N HCl to the phenolphthalein end point.

**Calculation.**—

$$\text{Alkalinity as NaOH, per cent} = \frac{\text{milliliters of HCl} \times N \times 0.40}{\text{weight of sample}} \times 100$$

ETHOXYL CONTENT <sup>69 70</sup>

**Apparatus.** Distillation Apparatus.—See Fig 41 30

**Oil Bath.**—Maintained at 145° to 150°C

**Reagents.**—Prepare the following reagents as prescribed, p 2093

**Potassium Acetate Solution.**

**Bromine Solution.**

<sup>67</sup> ASTM Standards, Pt 8, D914 50, ASTM, Philadelphia, 464, 1958

<sup>68</sup> ASTM Standards Pt 8, D914 50, ASTM, Philadelphia, 465, 1958

<sup>69</sup> ASTM Standards, Pt 8, D914 50, ASTM Philadelphia 466, 1958

<sup>70</sup> Samsel, E. P., The Dow Chemical Co., unpublished data

Sodium Acetate Solution.

Dilute Sulfuric Acid.

Hydriodic Acid, 57%.

Formic Acid, 90%.

**Procedure.**—Dry the sample at 105°C. for 30 min. Add 3 ml. of water to the scrubbing trap, *B*, and 10 ml. of bromine-acetic acid solution to receiver, *A*; then attach the receiver to the distillation apparatus (Fig. 41-30). Weigh 40 to 50 mg. of the dry sample into a No. 0 gelatin capsule, and drop into the boiling flask, *C*. (The weighing should be done as quickly as possible without sacrificing accuracy, because dry ethyl cellulose picks up moisture rapidly.) Add 2 ml. of melted phenol, a few silicon carbide chips to prevent bumping, and 6 ml. of constant boiling hydriodic acid. Attach at once to the distillation apparatus, using a few drops of HI to moisten the ground-glass joint.

Connect the side-arm of the flask to a source of nitrogen, and pass a current of the gas through the apparatus at a rate of 2 bubbles per sec. Immerse the flask in an oil bath maintained at 150°C., and react for 40 min.

Wash the contents of the receiver into a 500-ml. Erlenmeyer flask containing 15 ml. of 22% sodium acetate solution, and dilute to 125 ml. with water. Add formic acid dropwise, with swirling, until the brown color of the bromine is discharged and then add 6 drops in excess. After 3 min., add 3 g. of potassium iodide and 15 ml. of 1% sulfuric acid, and titrate the liberated iodine with 0.1 *N* sodium thiosulfate, using starch indicator solution near the end point. Carry the reagents through the same procedure.

**Calculation.**—

$$\text{Ethoxyl, per cent} = \frac{(A - B)C \times 0.00751}{D} \times 100$$

where *A* = milliliters of Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> solution required for titration of the sample,

*B* = milliliters of Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> solution required for titration of the blank,

*C* = normality of the Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> solution, and

*D* = weight of sample in grams.

#### VISCOSITY OF 5% SOLUTION<sup>71,72</sup>

**Principle.**—The sample is dissolved in a solvent and the viscosity of the solution is determined at 25°C. in a modified Ubbelöhde viscosimeter. For ethyl cellulose containing 45 to 47% ethoxyl, the solvent should be a 70:30 benzene-methanol solution. For ethyl cellulose having an ethoxyl content of 47% or more, the solvent should be an 80:20 toluene-ethanol solution.

**Apparatus.** Ubbelöhde Viscosimeter (Fig. 41-32).—The viscosimeter should have a capillary size so that at least 30 sec. is required for the solution to pass between the 2 calibration marks. Appropriate capillary sizes range from about 1.45 mm. for 10-centipoise solutions to 3.12 mm. for 200-centipoise solutions.

**Mechanical Shaker.**

**Constant Temperature Bath.**—Operating at 25° ± 0.1°C.

**Reagents.** 70:30 Benzene-Methanol.—Weigh 2100 g. of A.R. grade benzene and 900 g. of absolute methanol into a 1-gal. bottle, and mix thoroughly.

<sup>71</sup> ASTM Standards, Pt. 8, D914-50, ASTM, Philadelphia, 469, 1958.

<sup>72</sup> Mapes, D. A., The Dow Chemical Co., unpublished data.

80 20 Toluene Ethanol—Weigh 2400 g of redistilled toluene and 600 g of absolute 2B ethanol into a 1 gal bottle and mix thoroughly

*Procedure*—Weigh exactly 3 g of ethyl cellulose which has previously been dried for 1 hr at 105°C into an 8 oz bottle and add 57 g of the correct solvent (either

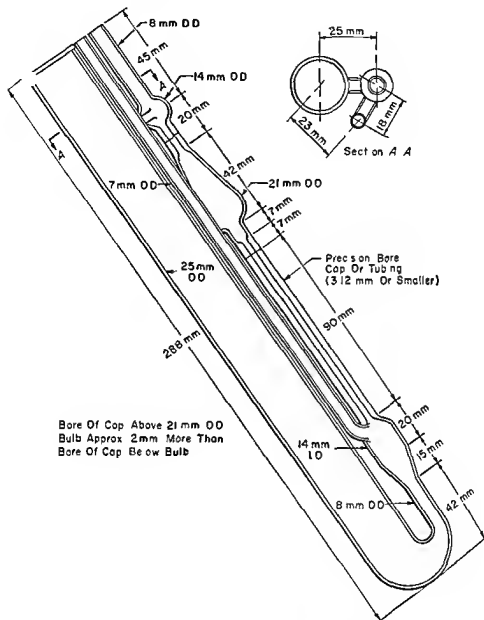


FIG. 41-32 Modified Ubbelohde Viscosimeter

of the 2 above) to make a 5% solution of the plastic. Place a piece of aluminum foil over the opening of the bottle and screw the cap on tightly. Place the bottle on the shaking machine and agitate until the sample is dissolved.

Transfer a portion of the solution to the Ubbelohde viscosimeter so that the

level of the liquid is just even with the bottom of the vent tube entrance. Place the viscosimeter in the constant temperature bath at  $25^{\circ} \pm 0.1^{\circ}\text{C}$ . When the solution attains the temperature of the bath, close the vent tube by placing a finger over the opening. Fill the calibrated part of the tube by exerting suction using a rubber bulb.

Open the vent tube. Measure the time in seconds required for the liquid level to pass between the 2 calibration marks. Duplicate flow-time measurements should agree within 0.2 sec.

Calculations.—

$$\text{Viscosity in centipoises} = \frac{T_1 \times D_1 \times n}{T_2 \times D_2}$$

where  $T_1$  = time of flow of unknown solution,

$T_2$  = time of flow of standard viscosity oil,

$D_1$  = density of unknown solution,

$D_2$  = density of standard viscosity oil, and

$n$  = *viscosity of standard viscosity oil in c.p.s.*

## Chapter 42

# POISONS

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This chapter presents selected procedures for the detection and estimation of certain poisons in body materials. Space limitation makes it necessary to cover only those substances which are most frequently responsible for the poisoning of human beings.

Most of the analytical methods presented are those which the authors have used for years with satisfactory results. Recent treatises on toxicology<sup>1, 2, 3, 4, 5</sup> list many alternate methods which are probably equally reliable.

### CHOICE AND HANDLING OF BODY MATERIALS FOR TOXICOLOGICAL ANALYSIS

**Living Subjects**—The materials commonly analyzed are blood, urine, saliva, breath and hair. For carbon monoxide one uses blood, in which about 0.3% of potassium oxalate is dissolved to prevent coagulation. Blood, urine, saliva, or breath may each be used for estimating the presence, and level, of ethanol or methanol in the body. The first three should be preserved by the addition of about 0.5% of sodium fluoride, which also serves as an anticoagulant for blood. Tests for mercury, lead, barbiturates, salicylates or alkaloids should employ blood or urine. In arsenic poisoning, the poison is found in urine or blood, and in delayed or chronic, arsenic poisoning this element accumulates in the hair and nails. For satisfactory results the analyst should be furnished with a minimum of 10 ml of blood or saliva, 100 ml of urine, and 0.5 g of hair or nails. Five ml of the fluids will suffice for ethanol or methanol.

**Autopsy Materials**—If possible, these should be obtained prior to embalming, because embalming introduces formaldehyde, methanol, and perhaps some other

<sup>1</sup> Bamford, F., *Poisons: Their Isolation and Detection*, 3d Ed., Revised by Stewart, C. P., Philadelphia, Blakiston, 1951.

<sup>2</sup> Kaye, S., *Handbook of Emergency Toxicology*, Springfield, Ill., Charles C Thomas Publisher, 1954.

<sup>3</sup> Gonzales, T. A., Lance, M., Helpern, M., and Ungerer, C. J., *Legal Medicine, Pathology and Toxicology*, New York, Appleton Century Crofts, 1954.

<sup>4</sup> Kaye, S., and Goldbaum, L. R., *Toxicology*, Chapter 24 in *Legal Medicine*, Ed by Gradwohl, R. B. H., St. Louis, Mosby, 1954.

<sup>5</sup> Stewart, C. P., and Stolman, A., *Editors and contributors of certain chapters, Toxicology: Mechanisms and Analytical Methods*, New York and London, Academic Press, Vol. I, 1960, Vol. II, 1961.



poisons, into the tissues. The organs submitted for analysis should always include: the stomach ligated at both ends and with no loss of contents, one kidney, about one-fourth of the liver (more in the case of a small child), blood from the heart or a large vein, and urine. A rib bone furnishes valuable evidence in suspected lead poisoning. In death from inhaled HCN, lung tissue contains the highest concentration of cyanide. In morphine poisoning the concentration in bile is many times greater than that in tissues, blood, or urine.

These autopsy materials should be placed in *clean* containers with tight lids. New fruit jars or paraffined cartons are satisfactory. To prevent diffusion of poison between samples, each sample should be stored in a separate container.

All samples from living or dead subjects should be labeled, sealed, and refrigerated. Storage in a deep-freeze will minimize later postmortem changes. At all times, the samples should be in the sole custody of a responsible person, whose testimony can trace the sample from its source to the analyst. Each tissue is weighed and run through a meat grinder and thoroughly mixed, or a weighed portion may be homogenized with a measured volume of water. The analyst should use only a portion of each sample, so that later check analyses may be performed, particularly if the first are questioned. If the quantity of stomach contents is too small for both the preliminary tests and the later systematic procedure, the preliminary tests should be omitted.

### PRELIMINARY TESTS

If any of these tests is positive, one can usually avoid the systematic procedure described in the section beginning on p. 2110.

### CYANIDE

*Procedure.*—Moisten one end of a narrow strip of filter paper with the modified Schonbein reagent (p. 2111), and shake the strip to remove excess liquid. Slightly open the jar containing the stomach and contents and expose the impregnated end of the strip to the jar air for about 15 seconds. Ingested cyanide will usually evolve sufficient HCN to produce a distinct blue color.

### FLUORIDE OR OXALATE

*Procedure.*—To about 5 g. of stomach contents add an equal volume of water, make slightly acid to litmus, and filter through a small fluted filter until clear. To the filtrate add a few drops of 5%  $\text{CaCl}_2$  solution. If no turbidity appears within a minute, toxic amounts of fluoride and oxalate are probably not present. If a precipitate appears, centrifuge in a conical tube, drain off the fluid, suspend the residue in 1:50 ammonia solution, again centrifuge and discard the fluid. Heat the residue with 2 ml. of 5%  $\text{H}_2\text{SO}_4$  and titrate with 0.01 *N*  $\text{KMnO}_4$ . Oxalate, if present, will cause a reduction of the permanganate.

To test for fluoride, transfer the contents of the centrifuge tube to a platinum crucible, add 0.5 ml. of 40%  $\text{NaOH}$ , and evaporate to dryness. Heat over a flame until no carbon remains. Cool, and conduct the etching test described on p. 424 of Vol. I, adding 2 ml. of concentrated  $\text{H}_2\text{SO}_4$  to the crucible just before covering it with the paraffined glass plate with a small 0 scratched through the paraffin. If toxic amounts of fluoride are present in the stomach contents, one will usually obtain a distinct etch on the glass plate.

**NOTE**—In fluoride poisoning 5 g of ashed tissues or blood do not usually contain sufficient fluoride to produce a visible etch by this method

### ARSENIC OR MERCURY

**Procedure (Reinsch Test)**—Obtain a piece of sheet copper about 0.015 in thick. Cut a three fourths inch square and place it in a beaker under a thin layer of water. By means of a pipet direct a stream of concentrated  $\text{HNO}_3$  on the surface of the strip until it is uniformly bright. At once drain off the fluid and rinse the strip with water leaving it covered with a little water. Add to the beaker 50 ml of water, 8 ml of concentrated  $\text{HCl}$  and 5 g of the stomach contents. Cover the beaker with a watch glass and boil the fluid gently for 15 minutes. Drain off the fluid, wash the strip twice with water and note any discoloration. No change usually rules out toxic amounts of arsenic or mercury. A black or brown stain may be due to arsenic, antimony, silver or bismuth. Mercury gives a gray silvery coating to the copper. Wash the strip with water, alcohol and ether and allow to dry. Roll the strip around a glass rod and slide it into a narrow Pyrex test tube. Heat the closed end of the tube in a flame for about one minute keeping the upper portion of the tube cool and holding it at an angle of about  $45^\circ$ . Note any sublimate on the tube above where it was heated. With mercury there may be a film of microscopic globules of the metal which can be seen under the microscope. If mercury is present vaporizing a tiny crystal of iodine in the tube will form red mercuric iodide. Arsenic is indicated by a white film of arsenic trioxide, the octahedral crystals of which may be identified by microscopic examination using high magnification. Pentavalent arsenic does not deposit readily on copper although a portion of it may be reduced to the trivalent state on boiling with organic matter.

### REDUCING VAPORS

**Reagents** Sulfuric Acid, Approx 16 N.—In a 125 ml flask place 40 ml of good distilled water. With shaking slowly add 30 ml of clear C P concentrated  $\text{H}_2\text{SO}_4$ . Cool. The solution should contain no impurities which will reduce permanganate. To test this add 1 drop of 0.05 N  $\text{KMnO}_4$  to 10 ml of the acid solution. The pink color should persist for at least 10 minutes. Some C P sulfuric acid does contain traces of such impurities.

**Permanganate** 0.05 N.—In a 100 ml volumetric flask place 0.158 g of C P  $\text{KMnO}_4$ . Add about 80 ml of double distilled water and shake vigorously until every particle of the permanganate is dissolved. Make up to 100 ml with water and place in a glass stoppered bottle. If stored in a dark place the permanganate will retain its strength for several months.

**Procedure**—Allow one of the jars of body material to warm to about room temperature. In a small glass bubbler tube place 5 ml of the 16 N sulfuric acid and add 0.1 ml of the 0.05 N permanganate. Connect a long glass ell to the bubbler tube inlet. Using an atomizer bulb with the valves reversed draw air from within the sample jar through the acid permanganate reagent keeping the jar covered as nearly as possible. If the tissue or fluid in the jar contains more than 0.1% of ethanol 5 bulbfuls (about 200 ml) of the air should discharge all of the purple color. Other alcohols and ether will also remove the permanganate color but acetone will not.

With urine the test can be conducted by using a second bubbler tube for aerat

ing the urine. To prevent foaming of the urine, add one drop of liquid petrolatum containing 6% of zinc stearate.

### ETHYLENE GLYCOL

*Procedure.*—Dilute 1 ml. of urine with 100 ml. of water. Test 1 ml. of the diluted urine, using the procedure described in ethylene glycol procedure for protein-free filtrate of blood or tissues (p. 2138). With urines containing much ethylene glycol, a strong red color will develop within 20 minutes. Normal urines will yield a faint red color when tested at 1:100 dilution.

### CARBON MONOXIDE

*Reagent.* Pyrotannic Acid.—In 50 ml. of water dissolve 0.5 g. of pyrogalllic acid and 0.5 g. of tannic acid. This solution will keep for a few days.

*Procedure.*—Dilute 1 ml. of whole blood with 9 ml. of water and mix. Add 10 ml. of the pyrotannic acid, stopper the tube, and shake for a few seconds. Observe at the end of 15 minutes. With normal blood the initial red color changes to a slate-gray, while blood containing CO-hemoglobin retains part, or all, of the red color, depending on the fraction of the hemoglobin bound with carbon monoxide. Oxalated blood gives a brighter color than does blood preserved with fluoride.

# SYSTEMATIC PROCEDURE FOR SEPARATING AND DETECTING CERTAIN POISONS FROM BODY MATERIALS

## VOLATILE POISONS

### STEAM DISTILLATION

*Apparatus*—An assembly of the type shown in Fig 421 is convenient. To facilitate back drainage of fluid which condenses in the Kjeldahl connecting bulb a second outlet from the distilling flask leads to a tube sealed to the side of the bulb. The upper end of the condenser tube is fitted with a two-hole rubber stopper, one hole of which carries the exit tube from the Kjeldahl connecting bulb and the second an ell which is normally closed by a clamped rubber tube. The ell is for introducing a little air to produce luminescence if yellow phosphorus vapor is evolved. To detect such luminescence the distillation must be conducted in a dark room or with the condenser enclosed in a light tight case. This test for phosphorus may be omitted and a portion of the distillate oxidized with bromine water and tested for phosphate as described on p 2144.

*Procedure*—Start the burner under the steam generator. Into a tared 500 ml Erlenmeyer flask weigh 50 g of hashed tissue or stomach contents and add about 60 ml of water and 1 g of solid tartaric acid.

*NOTE*—If a general unknown for poisons is being run one may save time by using a 50 g composite of stomach and contents liver kidney etc carefully weighing each portion.

Connect for distillation and pass a rather rapid current of steam into the distilling flask heating the flask with a low flame. At the moment the flask contents begin to boil lower the flame under the steam generator to minimize foaming which should subside within 5 minutes. Then the steam current is increased to produce rather rapid distillation. Collect about 90 ml of distillate. Run about 5 ml of water through the condenser tube and make the distillate up to 100 ml.

Most volatile poisons will be carried over quantitatively in the first 90 ml of distillate. However if phenols or chloral are found it will be necessary to resume the distillation and continue until a small fraction of the distillate shows no more of the substance.

*NOTE* Some works on toxicology recommend a further distillation of the tissue suspension after making it alkaline to remove volatile bases. This is very time consuming because the alkaline material foams badly and quantitative separation of some of these bases requires a very large volume of distillate. We have found chloroform extraction a much simpler procedure for separating such bases.

## QUALITATIVE TESTS ON THE DISTILLATE

Small aliquots of the distillate are used for these tests. If a given poison is found it is then determined quantitatively, using a larger aliquot of the distillate. Quantitative procedures are given in the section beginning on p. 2124.

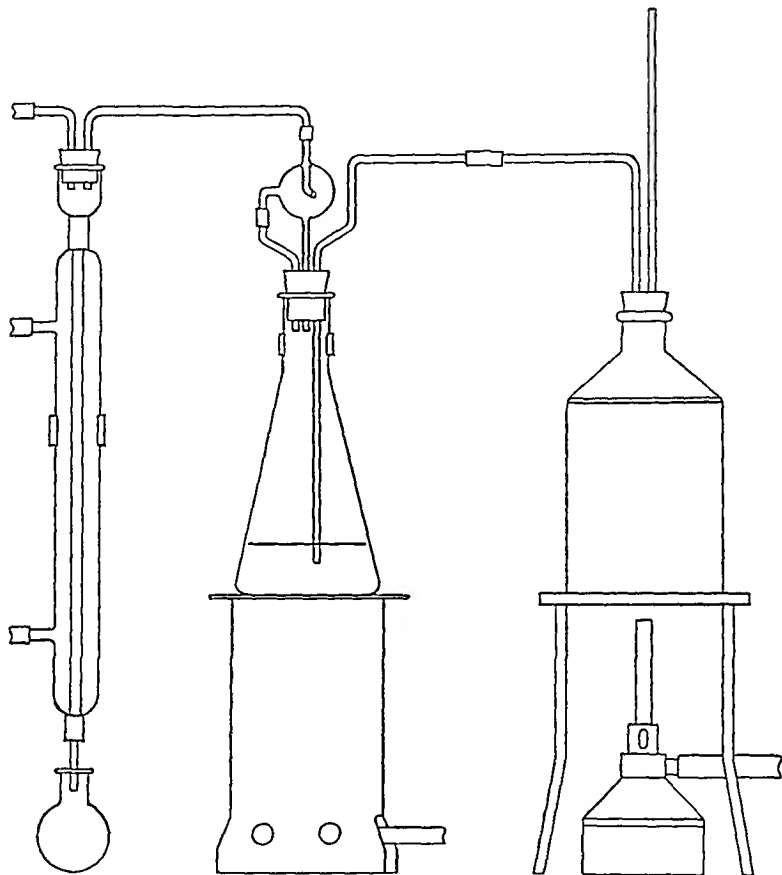


FIG. 42-1. Assembly for Steam Distillation of Body Materials. The Left Inlet at the Top of the Condenser Is Ordinarily Closed with a Clamp.

## CYANIDE

**Modified Schonbein Test.**<sup>6</sup> Reagent.—Weigh out approximately 50 mg. of finely powdered gum guaiac and shake in a stoppered flask with 25 ml. of 95% ethanol. Transfer 10 ml. of the supernatant fluid to a second flask and add 3 ml. of 0.1% copper sulfate in water containing 3 ml. of 1.0 N  $\text{H}_2\text{SO}_4$  per liter.

NOTE—We have found that the added trace of acid helps to prevent a false positive reaction. The reagent retains its sensitivity for at least 24 hours, but the alcoholic solution of gum guaiac deteriorates in a few hours. Some samples of gum guaiac function better than others.

<sup>6</sup> Sundberg, T., *Svensk. Kem. Tids.*, 33, 1112, 1921; *Chem. Abs.*, 15, 3431, 1921.

**Procedure**—Cut a strip of ordinary filter paper about 1 cm wide and 8 cm long. Moisten one end with the Schonbein reagent and shake off any excess fluid. Prepare this just before the first drop of distillate falls from the condenser insert the moistened end of the strip into the receiving flask and hold it near the falling drops for about 20 seconds. If  $\text{HCN}$  is being evolved the reagent on the strip will turn blue. Air containing 50 p p m (50 micrograms per liter) of  $\text{HCN}$  will give a strong blue color in 5 seconds and as little as 5 p p m will give a faint blue color in 20 seconds.

If the Schonbein test is positive at once add 1 ml of 10%  $\text{NaOH}$  to the receiver and raise it so that the end of the condenser dips into the fluid. Continue the distillation until about 90 ml of distillate has collected. Rinse the condenser tube and make the distillate up to 100 ml.

**Prussian Blue Test Procedure**—Place 5 ml of the distillate in a test tube and add 0.5 ml of 10%  $\text{NaOH}$ , 3 drops of approximately 5% ferrous sulfate solution (freshly prepared) and 2 drops of 10% ferric chloride solution. Heat almost to boiling for about one minute. Cool somewhat, add 4 drops of concentrated  $\text{HCl}$  and mix. The  $\text{HCl}$  will dissolve the iron hydroxides and if cyanide is present the fluid will assume a distinct blue color. On standing the Prussian Blue (ferric ferrocyanide) will usually precipitate. This also is a sensitive test.

### FORMALDEHYDE

Embalmed tissues and blood from an embalmed body contain formaldehyde and also methanol which always accompanies formaldehyde.

**Schiff Elvove Test<sup>7</sup> Reagent**—Place in a 200 ml flask 0.2 g of rosaniline (fuchsin) and add 120 ml of boiling water. Shake well until solution is complete. Cool and add 2 g of sodium bisulfite (meta) dissolved in 20 ml of water and mix. Add 2 ml of concentrated  $\text{HCl}$  dilute to 200 ml and again mix. The reagent becomes almost colorless in about one hour. Place in a glass stoppered bottle and store in a refrigerator. It will keep well for at least one month.

**Procedure**—To 3 or 4 ml of the distillate add 2 ml of the Schiff Elvove reagent. If no red color develops within 15 minutes formaldehyde is absent. If formaldehyde is present it will interfere with the tests for methanol and ethanol listed below and they should be omitted. There are methods for removing the formaldehyde and then estimating methanol and ethanol in the distillate but unless the embalming materials used to preserve the body are shown to contain no ethanol there is no point in trying to estimate ethanol or methanol.

### ACETONE

**Legal Test Procedure**—Place in a small test tube a few milligrams of powdered sodium nitroferricyanide (nitroprusside) and add 3 ml of the distillate. Shake to dissolve the powder which will give a faint brown color to the fluid. Add 2 drops of 50%  $\text{NaOH}$  and mix. In the absence of acetone the alkali will produce a yellow color. The presence of acetone causes the appearance of a strong orange color which fades within about 5 minutes.

**Acetest Procedure**—This is a modification of the Legal Test employing a white tablet (Cat No 2381 Ames Co. Elkhart Ind.). Place an Acetest tablet on a piece of white paper. Moisten with 2 drops of the distillate and observe at the end of 30 seconds. Acetone produces a color varying from light lavender to deep purple.

<sup>7</sup> Wright, I. O. J. Ind. Hyg. Chem. 19:750, 1927.

## SEPARATING AND DETECTING CERTAIN POISONS 2113

**Deniges Test.** Reagent.—In a flask place 4 g. of yellow mercuric oxide and 32 ml. of water. While shaking, add 16 ml. of concentrated  $\text{H}_2\text{SO}_4$ , followed by 32 ml. of water. When clear, place in a glass-stoppered bottle.

Procedure.—To 1 or 2 ml. of the distillate add two volumes of Deniges' reagent. Heat to about  $90^\circ\text{C}$ . for 5 minutes. A white precipitate indicates acetone, either preformed or from the decomposition of isopropyl alcohol. In ketosis, some acetone is present in the body.

### VOLATILE REDUCING SUBSTANCES

**Procedure.**—(Omit if formaldehyde is present.) Transfer 2 ml. of the distillate to a test tube and dilute with 3 ml. of water. Add 1 ml. of 0.0434  $N$   $\text{K}_2\text{Cr}_2\text{O}_7$  solution (see Ethanol, p. 2136). Next, add 5 ml. of concentrated  $\text{H}_2\text{SO}_4$  and mix by stirring with a glass rod ending in a ring at right angles with the rod. Run a blank with 5 ml. of distilled water. If the unknown does not show a decrease of yellow color, this rules out ethanol, methanol, and other reducing substances. If the 50 g. of body material which was steam-distilled contained more than 0.05% of ethanol or 0.023% of methanol all of the yellow color will disappear, leaving the green color of chromic sulfate.

### METHANOL

**Wright-Elvove Test.**—(Omit if the distillate contained formaldehyde.) In this test methanol is converted to formaldehyde, which yields a red to violet color with the Schiff-Elvove reagent. We have found that the presence of a small amount of ethanol results in a much more intense color. Ethanol alone gives no color.

**Reagents.** 14% Ethanol.—Dilute 15 ml. of 95% ethanol with distilled water to a volume of 100 ml.

**Acid Permanganate.**—Add 15 ml. of phosphoric acid (ortho, syrupy) to 90 ml. of water and dissolve in it 3 g. of  $\text{KMnO}_4$ . Transfer to a glass-stoppered bottle and store in a refrigerator. It will function well for several months.

**Oxalic Acid in 16  $N$   $\text{H}_2\text{SO}_4$ .**—Slowly pour 50 ml. of concentrated  $\text{H}_2\text{SO}_4$  into 62 ml. of water, while stirring the latter. Cool, and dissolve in it 5 g. of oxalic acid. Store in a glass-stoppered bottle. It will keep indefinitely.

**Schiff-Elvove Reagent.**—See formaldehyde test, above.

**Procedure.**—In a test tube place 2 ml. of the distillate. Add 0.2 ml. of the 14% ethanol and 1 ml. of the acid permanganate. Mix and allow to stand for 10 minutes. Reduce the excess of permanganate and  $\text{MnO}_2$  by adding 1 ml. of the oxalic-sulfuric acid solution and shaking the tube. As soon as the fluid clears add 2 ml. of the Schiff-Elvove reagent and mix. Examine at the end of 30 minutes. If methanol was present the fluid will assume a violet or pink color.

### ETHANOL

**Oxidation to Acetaldehyde.**—(Omit if formaldehyde or methanol is present.) In the absence of formaldehyde and methanol a reduction of dichromate in the test described above usually indicates the presence of ethanol.

**Apparatus.** *Copper Spiral.*—Obtain an 18-in. length of 16- or 18-gauge copper wire. Form a spiral at one end by coiling the wire around a  $\frac{5}{16}$ -in. rod, making about 8 turns with a small space between turns. Bend the straight portion so that it is in line with the spiral, and make a loop at the end to serve as a handle.

**Schiff-Elvove Reagent.**—(See formaldehyde test, above.)

*Stannous Chloride Solution.*—Dissolve 10 g. of C.P. stannous chloride crystals in 25 ml. of concentrated HCl. Place in a glass-stoppered bottle and store in the dark. It will keep well. For use, dilute 0.2 ml. with 40 ml. of water.

*Procedure.*—Transfer 20 ml. of the distillate to an evaporating dish and add an equal volume of saturated bromine-water. Evaporate to dryness and dissolve the residue in 5 ml. of 5%  $\text{H}_2\text{SO}_4$ . To 3 ml. of the solution add 1 ml. of the molybdate-sulfuric acid solution, quickly followed by 1 ml. of the dilute stannous chloride solution. As little as 2 micrograms of phosphorus will produce a blue color; 10 micrograms will give a strong blue color. If a blue color develops, reserve the remaining solution for quantitative estimation as described on p. 2144.

### CHLOROFORM-SOLUBLE POISONS

The classical procedure for isolating acid, basic, and neutral organic compounds from body tissues and fluids is to extract the finely-divided materials successively with 50%, 90%, and absolute, alcohol, discarding the undissolved material after each extraction. The final, absolute alcohol, extract is evaporated to a syrup and the residue is dissolved in a little water. The water solution is then shaken with a series of immiscible solvents, first while acid, and later, after being made alkaline. This procedure takes much time and uses a large amount of alcohol.

We have found<sup>9</sup> that chloroform extraction of the aqueous portion of the residue remaining after steam-distillation provides a very simple and much shorter method, which gives greater purity and a better yield of the compounds extractable by immiscible solvents. Most of the tissue lipids are eliminated by centrifuging the hot residue from the steam-distillation, prior to separating the aqueous phase. This aqueous fraction and chloroform are placed in a large, flat dish, which is slowly tilted back and forth through an arc of about 6°. The gentle, continuous movement of the two thin layers facilitates equilibrium of dissolved materials, with almost no formation of emulsions. Stomach contents and urine may be extracted directly. The tilter may be driven by a geared-down electric motor, but a float moved by a slowly oscillating water level is much simpler and more easily controlled.

*Extraction Apparatus. Water-Driven Tilter.*—This is shown in Fig. 42-2. A wooden platform, 11.5 inch square (1) is supported along its middle by a horizontal, free-moving shaft. An arm (2) extending from one end of the platform is attached to a vertical rod which ends in a cylindrical float (3) 2.5 inch high and 2.5 inch in diameter. This float moves freely up and down inside a slightly larger metal cylinder (4) which is about 4.5 inch high and 3 inch inside diameter. A slow stream of water enters cylinder (4) near its base and leaves from an outlet on the opposite side through a short siphon. The outlet is a 1-inch length of five-eighths inch brass tube, placed about 1.5 inch above the bottom of cylinder (4). The siphon tube fits loosely inside the brass tube, with a short sleeve of rubber tubing making the joint water-tight. The glass siphon (5) has a vertical loop which rises above 1.5 inch above the outlet tube. At a point where the descending limb of this loop is level with the metal outlet tube, the siphon tube is bent at an angle of 135° to the plane of the loop, and the siphon tube ends about 2.5 inch below this point. When the flow of water through the inlet is less than the speed of flow through the siphon, this causes cylinder (4) to fill and empty intermittently, in the manner of a Soxhlet extractor. If the ratio of inlet flow is about half that

<sup>9</sup> Harger, R. N., and Forney, R. B., *J. Pharmacol. Exptl. Therap.*, 98, 12, 1950.



of the siphon the float will rise and fall at a fairly uniform speed. If the flow through the inlet is too slow the siphon will not start and if too fast, the siphon stream will not break. Breaking of the siphon stream is facilitated by the  $135^\circ$  angle and the short length of the tube beyond this point. The siphon empties into a convenient drain.

The arc through which the platform tilts is controlled by a short metal arm (6)

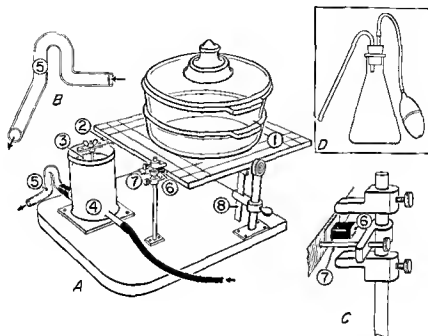


FIG. 42.2. Water-Driven Tilting Extractor for Immiscible Solvents. *A*, Complete Assembly. 1, Tilting Platform; 2, Arm Attached to Float; 3, Float; 4, Metal Cylinder; 5, Glass Siphon; 6, Short Arm Moving Between 2 Metal Stops; 7, Locking Pin; 8, Vertical Spring to Compensate for Shifts in Liquid. *B*, Enlarged View of Siphon. *C*, Enlarged View of Short Arm Moving Between Stops and Locking Pin. *D*, Suction Flask for Removing Fluid Layers.

which moves between two metal stops clamped to a vertical rod attached to the base of the apparatus. Also attached to this vertical rod is a sliding metal pin (7) which is used to lock the platform in a horizontal position when adding or removing the liquid layers in the flat dish.

A flat weight is fastened to the lower side of the tilting platform near the end farthest from the float having a weight which will not quite balance the weight of the metal arm and float.

To compensate for the shift in weight when the dish tilts and the liquids flow to one end of it, a straight piece of rather stiff metal spring (8) is rigidly attached to the supporting shaft and vertical to the plane of the platform. The lower portion of the spring is held in the slot of a movable arm which is clamped to one of the vertical supports holding the shaft bearing. The tension formed by bending this spring may be varied by raising or lowering the movable arm containing the slot. When using more than one extraction dish the tension on this spring must be increased.

The flow of water should be regulated so that the tilter makes from 6 to 10 complete excursions per minute, which represents a water flow of 1 to 2 liters per minute. Since a large portion of the chloroform used is recovered by distillation, the condenser for this purpose may advantageously be placed between the water supply and cylinder (4).

**Flat-Bottomed Dishes.**—These should have an inside diameter of 8 or 9 inches, with rather shallow sides. Crystallizing dishes are satisfactory but somewhat expensive. Pyrex baking dishes No. 221 are cheaper and function quite well. Since they stack easily, two or three of them may be tilted at one time. Only one lid is needed during the extraction.

**Suction Flask for Separating Liquid Layers.**—(Fig. 42-2,D). A 200-ml. Erlenmeyer flask is fitted with a 2-hole rubber stopper. One hole carries a glass U-tube bent at an angle of about  $45^\circ$ , one limb of which is about  $2\frac{1}{2}$  in. long and the other 6 or 7 in. long. The short limb extends through the rubber stopper for about three-fourths inch. The other stopper hole carries a straight glass tube about 2 in. long. By applying gentle suction to the short tube, one can collect through the longer tube all of the chloroform layer following an extraction. To avoid using the mouth for this purpose, one should employ an ordinary atomizer bulb with the valves reversed.

**Separatory Funnels.**—Pyrex, Squibb Type, 125 ml. (Corning No. 6400) are satisfactory. Use water only for lubricating the stopcocks.

**Preparation of Samples for Extraction. Urine.**—This may be extracted directly, using 50 to 100 ml.

**Stomach Contents.**—A sample weighing 20 to 50 g. is used. If it is very viscous, water is added until it will flow freely. Direct extraction is then carried out.

**Tissues.**—The flask containing the residue from the steam-distillation is reweighed and the weight of its contents obtained by difference. A Hanson Diet Scale of 500 g. capacity is convenient for this purpose, since one may shift the dial to allow for the weight of the flask. If not still hot, the flask contents are again heated to boiling. The hot suspension is immediately transferred to a 250-ml. salt-mouth bottle and centrifuged at about 1200 r.p.m. for 5 minutes. This separates the suspension into a packed layer of tissue at the bottom, an aqueous layer, and a small layer of melted fat at the top. The aqueous layer, which usually comprises about two-thirds of the total material in the bottle, is then drawn off by means of the suction flask (Fig. 42-2,D) and weighed. Mouth suction is advised for separating this aqueous layer, and one should apply a faint pressure when the inlet tube penetrates the fat layer. The aqueous portion is now ready for extraction.

Since the solid layer of packed tissue is mostly water, this means that the concentration of any alkaloids or neutral compounds is about the same in the aqueous fraction as in the total residue from the steam-distillation. With barbiturates the concentration is much greater in the fat layer, but since this layer is usually a very small per cent of the total, the major part of barbiturates will be dissolved in water.

**Chloroform Extraction. Extraction at pH 9.**—Place the fluid, usually measuring 50 to 150 ml., in the extraction dish. While rotating the fluid in the dish, add strong ammonia water, dropwise, until a pH of approximately 9.0 is reached, as shown by tests with Hydrion paper. If the fluid becomes too alkaline, add the necessary amount of strong HCl.

Lock the tilter platform in the horizontal position and set the stops controlling the movement of arm (6) so that there is a space of about 7 mm between this arm and each of the stops. Place the dish on the locked platform and tilt the dish toward the operator by placing a small block under the end of the dish opposite him. Slowly pour 100 ml of chloroform on the exposed part of the dish bottom so that it flows smoothly beneath the aqueous fluid. Remove the block, cover the dish and center it on the platform. Start the flow of water and withdraw the lock pin. Regulate the water flow so that the siphon operates intermittently. If the short arm (6) does not move the full distance between the two stops, shift the dish slightly to the left or right to produce proper tilting of the platform.

Operate the extractor for 30 minutes at a tilting speed of about 8 complete excursions per minute. At the end of this time lock the platform in the horizontal position, tilt the dish forward by means of the block and allow the two fluids to separate for a few minutes. Using the suction flask, remove the chloroform layer, employing the modified atomizer bulb for suction and pinching the connecting rubber tube before squeezing the bulb. With a little practice one can completely remove the chloroform without bringing over more than a few ml of the aqueous portion.

Transfer the chloroform extract to a 125 ml Squibb separatory funnel having a well ground stopcock which is lubricated only with water. Allow any water present to rise to the surface and filter the chloroform extract through a dry paper into a 300 ml Erlenmeyer flask. Return the water portion to the dish and repeat the extraction with another 100 ml of chloroform. At the end of 30 minutes of tilting, separate the second chloroform extract and filter it into the flask containing the first extract. Further treatment of the combined extracts is described in the section below.

**Extraction at pH 6**—To the aqueous fluid in the extraction dish add strong HCl dropwise until the fluid reaches a pH of about 6.0. Extract this fluid with 100 ml of chloroform for 30 minutes, separate the chloroform and filter it into a second 300 ml flask. Save this extract for further operations described in the next section.

**Treatment of Chloroform Extracts** Extract from Aqueous Fluid at pH 9.—Recover most of the 200 ml of chloroform from the extraction at pH 9 using corks (not rubber stoppers) to connect the tube from the flask to the condenser. Place two glass beads in the flask and distill until about 10 ml of chloroform remain in the flask. Do not heat to dryness. Transfer the concentrated chloroform extract to a 90 mm glass evaporating dish and use small portions of chloroform to rinse out the flask and add the rinsings to the dish. Add 3 drops of concentrated HCl to prevent loss of any nicotine and evaporate to dryness on the steam bath. Note the quantity and appearance of any residue in the dish. This residue represents any alkaloids originally present in the aqueous layer on the tilter except part of the morphine plus most of any barbiturates in this layer.

With the dish still warm, add 5 drops of concentrated HCl, rotating the dish to moisten the inner surface with the acid. Add about 15 ml of water and heat on the steam bath for 15 minutes, stirring occasionally with a short glass rod. Place the dish in a layer of ice water for about 5 minutes in order to solidify any fat droplets present. These droplets will usually adhere to the sides of the dish so that the fluid may be separated by decantation.

Select a 60 ml Squibb separatory funnel with a well ground stopcock. Lubricate this stopcock with water only. Decant the fluid in the dish into the separa-

tory funnel and rinse the dish with two 1-ml. portions of water, adding the rinsings to the funnel. Shake the liquid in the funnel with an equal volume of ether. Drain the aqueous layer into a small flask, pour the ether portion back into the evaporating dish and evaporate it. If a noticeable residue remains in the dish, repeat the extraction with ether and evaporate this second ether extract in the same dish. Place 1 ml. of water in the separatory funnel, stopper and shake, and add this to the acid solution in the flask.

Rinse the separatory funnel and its stopcock joint with distilled water, to remove all traces of acid. Return the aqueous solution to the separatory funnel and add strong ammonia water, dropwise, until a pH of about 9.0 is reached. Shake out twice with 10-ml. portions of chloroform. Pass the chloroform extracts through a small dry filter, collecting the filtrate in a weighed glass evaporating dish. Add 2 drops of concentrated HCl and evaporate to dryness. Record the weight of any residue obtained and observe its appearance. Save it (Fraction *A*) for the qualitative tests for alkaloids described in the following section, and for quantitative determinations listed in the section, Alkaloids, on pp. 2124 and 2125.

**Extract from Aqueous Fluid at pH 6.0.**—Distill off most of the chloroform from this extract and transfer the concentrated extract to the dish containing the ether soluble extract from the preceding section. Evaporate to dryness, cool, and observe any residue in the dish. Barbiturates, if present in appreciable amounts, frequently crystallize at this point.

To remove any fat which may be present, use the method of Cheramy and Lagarge.<sup>10</sup> To the contents of the dish add about 5 ml. of strong ammonia water and 20 ml. of water. Heat on the steam bath for 15 minutes, stirring at intervals with a short glass rod. Transfer the hot fluid to a weighed Erlenmeyer flask and record the weight of fluid. At once, add 5 ml. of 10%  $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$  solution, stopper the flask, and shake well. Any fat present will precipitate as barium soaps plus fat. Filter, while still hot, through a small fluted paper. The material usually filters rapidly, giving a clear filtrate. Collect the filtrate in a weighed flask and record its weight, which represents an aliquot of the total including the barium chloride solution added.

Re-wash the separatory funnel and transfer the filtrate to it. Add concentrated HCl dropwise until the fluid is distinctly acid to litmus. Allow to cool somewhat, and extract twice with 10-ml. portions of ether. Pass the ether extracts through a dry filter paper and evaporate to dryness in a weighed glass dish. Record the weight of any residue obtained and note its appearance. Save it (Fraction *B*) for tests for barbiturates, etc., given on p. 2122, and in the section on p. 2130.

## QUALITATIVE TESTS FOR COMPOUNDS EXTRACTABLE BY CHLOROFORM

### ALKALOIDS: GENERAL PRECIPITATION TESTS

**Preparation of Solution.**—Dissolve the residue in the weighed dish containing Fraction *A* in dilute HCl, stirring well to complete solution. Add ammonia water dropwise to give a pH of about 9.0; extract twice with chloroform, and make up the total extract to a volume of 25 ml. Use small aliquots of this (Solution *A*) for the tests below.

<sup>10</sup> Cheramy, P., and Lagarge, J., *J. pharm. chim.* (8) 12, 366, 1930; *Chem. Abs.*, 25, 894, 1931.

**Reagents**—There are many alkaloid precipitants. They are not specific for alkaloids but a negative result usually rules out toxic quantities of most alkaloids. Three precipitants are listed.

**Phosphotungstic Acid**—Dissolve 20 g of sodium tungstate and 14 g of disodium phosphite in 100 ml of water and add concentrated  $\text{HNO}_3$  until the solution is distinctly acid to litmus.

**Wagner's Reagent**—This is 0.1 N iodine in 18% KI prepared as usual.

**Silicotungstic Acid**—Dissolve 10 g of the compound in 100 ml of water.

**Procedure**—Take 5 ml of the Solution A and shake with 3 ml of distilled water to remove traces of ammonia which will interfere with the test for nicotine. Filter the chloroform layer through a dry paper into an evaporating dish. Shake the aqueous layer with 3 ml of chloroform and filter the chloroform into the dish. Add 1 drop of concentrated HCl to the dish and evaporate the contents to dryness. Dissolve the residue in 3 ml of 0.1 N HCl.

Place 0.5 ml portions of the HCl solution in three narrow test tubes. To one add 1 drop of the phosphotungstic acid solution and to the second add 1 drop of Wagner's reagent. The absence of a turbidity or precipitate in both tests usually rules out alkaloids. If these are negative one can omit the later tests for alkaloids except those for nicotine, strychnine, and morphine.

To the third tube add 1 drop of the silicotungstic acid solution. Nicotine gives a white turbidity later becoming crystalline.

Save the remaining HCl solution for certain later tests.

### STRYCHNINE

**Fading Purple Test**—Place 2 ml of Solution A in a small porcelain evaporating dish having a round bottom and evaporate to dryness. Add 0.5 ml of concentrated  $\text{C.P. H}_2\text{SO}_4$  and stir with a glass rod to effect solution. Add a small crystal of  $\text{K}_2\text{Cr}_2\text{O}_7$  and rotate the dish to bring the acid in contact with the dichromate. Strychnine yields a play of colors: blue, violet, purple, orange.

**Taste**—Apply a few drops of the HCl solution used in the alkaloid precipitation tests to the tip of the tongue. Strychnine gives an intensely bitter taste which persists for at least 15 minutes. Quinine also tastes bitter but the degree is much less and the acid taste is soon gone. Save the remaining solution for the Frog Test.

**Frog Test**—Perform only if the Fading Purple and Taste Test above are positive. To 0.5 ml of the HCl solution used in the Taste Test add 0.1 ml of 0.1 N  $\text{NaOH}$ . Obtain a lively frog weighing about one ounce. While holding the animal by the hind legs inject 0.5 ml of this solution into the lymph sac immediately beneath the skin of the back at the root of the legs. Place the frog in a large closed glass jar moistened with water and observe for one hour. One microgram of strychnine per gram of frog will usually produce typical convulsions within 30 minutes with the frog's hind legs kept rigidly extended.

**Extraction by Chloroform from 10 N HCl**—Unlike most alkaloids except heroin, strychnine is extractable from 10 N HCl by chloroform, the distribution ratio being about 55:45 for 10 N HCl:chloroform.<sup>2</sup> The corresponding ratios for pH 2, pH 3, and pH 4 are respectively 97:3, 97:3, and 73:27. Thus shaking 10 ml of 10 N HCl containing strychnine with 20 ml of chloroform will transfer about 65% of the strychnine to the chloroform phase. This property may be used to separate strychnine from many other organic bases including quinine (perform only if the original chloroform solution gave the fading purple reaction). Add 5 ml of pure chloroform to 1 ml of Solution A above and shake with 3 ml of

1.0 N HCl. Filter the chloroform layer, evaporate to dryness, and try the Fading Purple Test with the residue. This residue should still give a positive reaction.

### MORPHINE AND DERIVATIVES

*Marquis Test.* Reagent.—To 3 ml. of concentrated C.P.  $\text{H}_2\text{SO}_4$  add 2 drops of U.S.P. formaldehyde solution and mix.

*Procedure.*—In a small round-bottomed porcelain dish place 2 ml. of Solution A and evaporate to dryness. To the residue add 2 drops of Marquis reagent. Morphine and heroin give a red color, changing to violet and then to blue. Codeine and dilaudid yield a violet color, but no initial red. Amphetamine and phenylethylamine give an orange precipitate.

*Separation of Heroin.*—Like strychnine, heroin is extractable by chloroform from 1.0 N HCl solution, the distribution ratio being about 60:40 for 1.0 N HCl:chloroform. Evaporate 2 ml. of Solution A to dryness and dissolve the residue in 5 ml. of 1.0 N HCl. Shake out twice with 10-ml. portions of chloroform. Filter the combined chloroform extracts through dry paper and evaporate to dryness in a small porcelain dish. A typical color reaction with Marquis reagent indicates heroin. Save the aqueous portion for the following test.

NOTE.—If heroin is found to be present, extract the aqueous portion a third time with chloroform to remove final traces of this alkaloid.

*Separation of Codeine.*—At pH 6.0 the water:chloroform codeine partition ratio is 40:60, while that of morphine is about 98:2. To the aqueous portion from the preceding section add 2 g. of sodium acetate crystals, and shake to give a pH of approximately 6.0. Extract twice with two volumes of chloroform. The residue from the evaporated chloroform extract should give a positive Marquis reaction if codeine is present. Save the aqueous portion for the next test.

*Separation of Morphine.*—At pH 9 the partition ratio of morphine between water and a 9:1 mixture of chloroform and ethanol is 51:49.

To the aqueous fraction from the preceding section add, dropwise, a strong ammonia solution to give a pH of about 9.0. Extract twice with two volumes of the 9:1 chloroform-ethanol mixture. Evaporate the chloroform-ethanol extract and test the residue with Marquis reagent. Morphine, if present, will give its typical color reaction of red, violet, and blue.

### COCAINE

*Taste Test.*—In the taste test (see under Strychnine, p. 2120) the presence of cocaine will produce numbness of the treated end of the tongue, and of the lips.

*Formation of Picrate.*—To the HCl solution remaining from the frog test for strychnine, add some saturated aqueous picric acid solution. If crystals form, examine them under the microscope and compare with the crystals formed by treating a weak, known solution of cocaine with picric acid.

### ATROPINE

*Vitali's Test.*—Place in a round-bottomed porcelain dish 2 ml. of the Solution A and evaporate to dryness. To the residue add 2 drops of fuming  $\text{HNO}_3$  and again evaporate to dryness. Cool, and add 2 drops of a freshly-prepared, strong solution of KOH in 95% alcohol. Atropine produces a marked violet color, soon changing to red, and then fading.

## NICOTINE

(See Precipitation Tests above) If silicotungstic acid produced a white precipitate this suggests nicotine

**Procedure**—Evaporate 1 ml of Solution A to dryness. Add a drop of ammonia solution and heat on the steam bath for 30 minutes. This should volatilize any nicotine and 0.1 N HCl washings from the dish should no longer yield a white turbidity on adding silicotungstic acid solution.

## QUININE

**Procedure**—The residue left on evaporating 1 ml of Solution A is dissolved in 2 ml of 5%  $H_2SO_4$ . If quinine is present the resulting solution will exhibit a strong blue fluorescence under ultraviolet light.

## CAFFEINE

While caffeine is not a poison it is often present in stomach contents and will appear in the alkaloid fraction.

**Murexide Test**—In a round bottomed porcelain dish place 1 ml of Solution A and evaporate to dryness. To the residue add 2 drops of concentrated HCl and a tiny crystal of  $KClO_3$ . Again evaporate to dryness. On moistening this residue with strong ammonia solution a bright purple red color is formed if caffeine is present.

## ACONITINE

In the taste test (see under Strychnine p 2120) aconitine will cause a peculiar tingling and numbing sensation of the tongue and lips.

If the beating exposed heart of a frog is moistened with an extremely dilute solution of aconitine the heart will stop with the ventricles contracted.

## BARBITURATES AND OTHER ACIDS—GENERAL TESTS

**Preparation of Solution**—Dissolve the ether soluble extract in its dish (Fraction B p 2119) in ether transfer to a glass stoppered cylinder and make up to 25 ml (Solution B). Use small aliquots of this solution for the following qualitative tests.

**Reaction with Millon's Solution** **Reagent**—Weigh 20 g of metallic mercury and transfer to a flask. Place the flask in a fume hood and add 14 ml of concentrated  $HNO_3$ . Allow to react until the evolution of brown fumes ceases. Dilute with 20 ml of water and allow any remaining mercury to settle. Transfer the aqueous fluid to a glass stoppered bottle.

**Procedure**—Place 2 ml of Solution B in a small round bottomed dish and evaporate to dryness. Add 0.5 ml of water and heat on the steam bath for 2 minutes. While still hot transfer 1 drop of the water extract to the center of a small watch glass. Place a drop of the Millon's reagent on the glass close to the first drop. Slowly tilt the glass to merge the two drops. If barbiturates are present a white turbidity will appear at the junction of the two drops and the turbidity will disappear when an excess of the Millon's reagent mixes with the other fluid. This is a very sensitive test. If it is negative toxic amounts of barbiturates are not present.

**Zwicker Test**<sup>11</sup> **Reagents** **Cobalt Nitrate Solution**—Dissolve 0.5 g of  $Co(NO_3)_2 \cdot 6H_2O$  in 50 ml of absolute ethanol and store in glass stoppered bottle. This solution keeps well.

<sup>11</sup> Zwicker J J L. Pharm Weekbl 68, 975 1931 Chem Abs 26, 396 1932

*Alcoholic KOH.*—Warm 0.5 g. of KOH pellets in 50 ml. of absolute ethanol until solution is complete. Cool, and store in a rubber-stoppered bottle.

*Procedure.*—Evaporate 2 ml. of Solution *B* and dissolve the residue in 3 ml. of absolute ethanol. Transfer 2 ml. of the solution to a small test tube and, while shaking, add 0.2 ml. of the cobalt nitrate solution followed by 0.2 ml. of the KOH solution. Most barbiturates yield a deep blue color, which fades somewhat in 5 minutes. The limit of sensitivity is about 0.1 mg. of barbiturate per ml. of the ethanol solution used. Thio-barbiturates do not respond to this test.

### DIFFERENTIAL TESTS FOR BARBITURATES

*Modified Ekkert Test.*—Evaporate 2 ml. of Solution *B* in a porcelain dish. Add 2 ml. of concentrated  $\text{H}_2\text{SO}_4$ . Stir and heat on the steam bath for 5 minutes. Add 2 drops of U.S.P. formaldehyde and mix slowly. Phenobarbital gives a pink color, changing to a mahogany shade. Amytal, pentobarbital, and several other barbiturates yield a yellow color. Barbital, ortal and neonal, give no color.

*Permanganate Oxidation.*<sup>12</sup>—Evaporate 2 ml. of Solution *B* and dissolve the residue in 3 ml. of 0.1 *N* NaOH. Add 0.5 ml. of 0.05 *N*  $\text{KMnO}_4$  (1.58 g. per l.) and mix. Unsaturated barbiturates, such as seconal, dial, and alurate, give an immediate green color, later changing to yellow-brown. As little as 0.1 mg. of these barbiturates will yield a greenish-purple.

*Melting Point.*—The barbiturate residue should usually be purified, preferably by sublimation. Evaporate in a tiny lipless beaker enough of Solution *B* to yield about 1 mg. of the barbiturate. Cover the beaker with a small watch glass and heat the beaker on the block of a thermostatically-controlled melting point apparatus, keeping a little water in the watch glass. Start with a temperature of about 150° and gradually increase the block temperature until sublimation begins, and maintain this temperature. Place a few crystals of the sublimate on a microscope cover slip and determine the melting point. Sublimation may also be performed by evaporating the ether solution in a 16-mm. soft glass test tube, using a current of air drawn past the surface of the ether by means of a glass tube clamped so that it is held about one-fourth inch above the liquid, and then heating the test tube in a paraffin bath fitted with an asbestos board cover, with the test tube connected to a good mechanical vacuum pump. When the sublimate has collected on the part of the tube above the asbestos board, the tube is removed, wiped clean, and the portion below the sublimate cut off by means of a hot Nichrome wire.

Most barbiturates, if present in Fraction *B*, will crystallize in time. Seconal is an exception; it practically always remains an oil. However, on flowing  $\text{CHCl}_3$  vapor over this oil, its surface will show transient crystallization, probably due to formation of an unstable seconal- $\text{CHCl}_3$  double compound.

### SALICYLIC ACID

In poisoning from aspirin or methyl salicylate the body will contain large amounts of salicylates, which will be found as salicylic acid in the extract containing the barbiturates.

*Color with Ferric Iron. Reagent.*—Dissolve 1 g. of  $\text{Fe}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$  in 100 ml. of water and add to the solution 0.5 ml. of concentrated  $\text{HNO}_3$ .

*Procedure.*—Evaporate to dryness 2 ml. of Solution *B*. Warm the residue with 3 ml. of water to effect solution. Cool, and add 1 drop of the ferric nitrate reagent. Salicylic acid yields a purple color.

<sup>12</sup> Hargreaves, G. W., and Nixon, H. W., *J. Am. Pharmaceut. Assn.*, 22, 1250, 1933.



# QUANTITATIVE DETERMINATION OF CERTAIN POISONS

If the qualitative tests described in the last section did not reveal any poison quantitative analyses for any of the poisons listed in that section are usually not indicated. With lead, no qualitative test was given and if lead poisoning is suspected the analyst should conduct the quantitative procedure. However, we should mention that traces of lead, arsenic and mercury are usually present in body materials from normal people, so the finding of such traces means nothing.

Most of the quantitative procedures described in this section involve the use of spectrophotometric measurements. Besides knowing how to operate these instruments the analyst should clearly understand *transmittance* (transparency) and *optical density* (O D), the relation between the two, and the formula for calculating concentration of the unknown from its O D and the O D of the standard used. To obtain best analytical results the concentration of the compound employed should give a transmittance between 25% and 80%, i.e. O D values between approximately 0.60 and 0.10 respectively. Where a visible color is used for the determination an ordinary photoelectric colorimeter operating between 400 and 800  $m\mu$  may be employed.

The poisons for which quantitative procedures are presented in this section are listed alphabetically with Alkaloids and Barbiturates each covering a group of compounds.

## ALKALOIDS

### PRELIMINARY APPROXIMATION

Where no alkaloid is present in the 50 g sample of body material which was carried through the procedure described in the last section, the weight of Fraction 1 is usually only about 0.5 to 2 mg. If the qualitative tests indicate a given alkaloid the weight of Fraction 1 in excess of 1 or 2 mg may give a rough estimate of the quantity of alkaloid present. This applies particularly to stomach contents where many milligrams of alkaloid may be recovered if death occurred soon after ingestion of the poison.

Some further idea of the quantity of alkaloid present may be obtained from the intensity of the color reactions, the yield from precipitation tests, and the degree of biological effects such as taste and frog tests with strychnine, when these results are compared with the results obtained by subjecting varying known amounts of the alkaloid to these tests.

### ULTRAVIOLET SPECTROMETRIC ANALYSIS<sup>2, 4, 5</sup>

Alkaloids, like many other organic compounds exhibit strong light absorption in the ultraviolet region. Thus, the O D of a 1 mg per cent solution of strychnine, at wavelength 255  $m\mu$ , exceeds the O D of the same concentration of  $KMnO_4$  at

the visible wavelength  $520\text{ m}\mu$ . These two wavelengths are the points of maximum light absorption for the two compounds. If we plot the O.D. of a given concentration of strychnine against wavelength in the range from 220 to  $350\text{ m}\mu$ , we obtain a curve which is typical for this compound. If the strychnine is dissolved in  $0.5\text{ N H}_2\text{SO}_4$ , its O.D. curve has a maximum at  $255\text{ m}\mu$  and a minimum at  $230\text{ m}\mu$ . The other alkaloids behave similarly, each giving its characteristic curve. When dissolved in  $0.5\text{ N H}_2\text{SO}_4$ , the alkaloids mentioned in the section on chloroform-soluble poisons exhibit the following  $\text{m}\mu$  wavelength maxima and minima, respectively: aconitine: 200, —; caffeine: 272, 247; cocaine: 233, 225; codeine: 286, 258; heroin: 280, 253; morphine: 285, 262; nicotine: 259, 230; quinine: 250, 230; and strychnine: 255, 230. With some of the alkaloids the curve has more than one hump, giving additional maxima and minima.

**Apparatus.**—The Beckman DU quartz spectrophotometer is widely used for this type of analysis. The cells for holding the fluid are made of fused silica with transparent windows, and have an internal, horizontal cross section of 1 cm. Cells of ordinary glass cannot be used for work in the ultraviolet range.

This type of spectrophotometer, equipped with an automatic recording device, saves much time in plotting the O.D.-wavelength curve of the solution being tested. However, this curve can be obtained with the Beckman DU instrument, but the 100% transmittance of the control fluid must be re-set for each change of wavelength.

**Procedure.**—Measure an aliquot of Solution *A* estimated to contain about 0.2 mg. of the alkaloid indicated by the qualitative tests. Evaporate to dryness, dissolve the residue in 3 ml. of  $0.5\text{ N H}_2\text{SO}_4$ , and make up to 5 ml. with the acid. (If nicotine is the alkaloid, add 1 drop of concentrated HCl before evaporating to dryness.) Place about 3 ml. of this acid solution of the alkaloid in one of the silica cells, and in a second cell place 3 ml. of the  $0.5\text{ N H}_2\text{SO}_4$ . Set the wavelength of the instrument at the point of maximum absorption for this alkaloid, which is given above. Adjust the transmittance of the cell containing the control to 100%, and read the O.D. of the unknown. Calculate the concentration of the alkaloid in the unknown by comparing its O.D. with an O.D. curve made by reading a series of standards containing 2 to 20 micrograms of the alkaloid per ml. of  $0.5\text{ N H}_2\text{SO}_4$ .

For further identification of the alkaloid, read the unknown at the minimum point of the O.D.-wavelength curve for the alkaloid, and also take readings with the wavelength set about  $5\text{ m}\mu$  on each side of the maximum of the O.D. curve for the alkaloid. While the complete O.D. curve is not absolutely essential, it does furnish valuable identification evidence.

## DETERMINATION OF MORPHINE IN URINE

If morphine is present in urine or tissues, a large portion of the alkaloid is combined, mostly with glucuronic acid, which compounds are not extractable in the immiscible solvents used. In the method for tissues described in the section beginning on page 2110, the heating with tartaric acid during the steam-distillation will free most of the morphine from the combined state. In analyzing urine for morphine one must first hydrolyze any morphine compounds present.

**Procedure.**—To 50 ml. of urine add 5 ml. of concentrated HCl and autoclave at 15 lbs. pressure for 30 minutes. Cool and adjust the pH to about 8.2 by the dropwise addition of 40% NaOH and testing with Hydrion paper. Add 25 ml. of

benzene and 25 ml of isobutanol and agitate in a mechanical shaker for 15 minutes. Allow the layers to separate and discard the aqueous layer. To the benzene isobutanol layer add 10 ml of 0.1 N HCl and shake for 15 minutes.

Aliquots of the acid layer may be evaporated to dryness and the residue tested for morphine by the qualitative procedures listed above (pp 2119-2123). The residue from another aliquot may be dissolved in 0.5 N  $\text{H}_2\text{SO}_4$  and read in the spectrophotometer as described above. However, unless the urine contains much morphine, other extractives will interfere with the spectrophotometric analysis and the qualitative tests. To separate the morphine from other extractives one should use paper chromatography or paper ionophoresis. Since a clear description of these two procedures is beyond the scope of this chapter, the reader is referred to Chapter 9, of this work and other publications<sup>4,5</sup> which deal adequately with these methods.

### SEPARATION OF MIXED ALKALOIDS

Fortunately, most cases of alkaloid poisoning involve but one compound but occasionally mixed alkaloids are encountered. Here the qualitative tests may help but the best solution is to use paper chromatography or paper ionophoresis, running parallel control spots of known samples of the suspected alkaloids.

## ARSENIC

### METHOD OF RAMBERG AND SJOSTROM<sup>13</sup>

Body tissues or fluids are completely wet ashed with  $\text{HNO}_3$  and  $\text{H}_2\text{SO}_4$  and any remaining  $\text{HNO}_3$  is destroyed by digesting with aqueous ammonium oxalate leaving arsenic in the pentavalent state. After diluting with water, concentrated HCl hydrazine sulfate, and a little bromide are added. The resulting  $\text{AsCl}_3$ , plus much of the HCl, are distilled and absorbed in water. A trace of methyl orange is added to the distillate, and the  $\text{AsCl}_3$  in it is titrated with  $\text{KBrO}_3$ . The methyl orange will be decolorized at the moment excess bromate is added.

**Apparatus**—This apparatus assembled for distillation, is shown in Fig 423. The 300 ml Pyrex Kjeldahl flask is connected to the air condenser by a 29/42 standard taper joint. The receiver is a 200 ml Erlenmeyer flask with file markings indicating volumes of 150 ml and 175 ml. The receiver is cooled in a beaker containing water. A stream of water enters the beaker at one side and leaves on the opposite side through a constant level siphon.

**NOTE**—For analyzing small samples we use a 100 ml Kjeldahl flask with 19/30 standard taper joint and a proportionally smaller air condenser. The receiver flask has a capacity of 125 ml, or 50 ml and is graduated at one half or one fourth of the volumes used for the large apparatus.

**Reagents**—All reagents must be arsenic free.

Sulfuric Acid, C.P.

Nitric Acid, C.P.

Hydrochloric Acid, C.P.

**Ammonium Oxalate Solution**.—Dissolve 20 g of C.P. ammonium oxalate in 500 ml of water.

<sup>13</sup> Ramberg, L., and Sjostrom, G. Report of Swedish Arsenic Commission Sec 8 1919 (In Swedish), Brahme, L., Acta Med Scandinav, Suppl V, 67, 1923.

**Hydrazine Sulfate.**—Eastman No. 575 has proved satisfactory.

**Potassium Bromide Solution.**—Dissolve 5 g. of KBr in water and make up to 50 ml.

**Potassium Bromate Solution.**—Dissolve 0.1485 g. of c.p.  $\text{KBrO}_3$  in water and make up to 1 liter. One ml. is equivalent to 0.2 mg. of As (element).

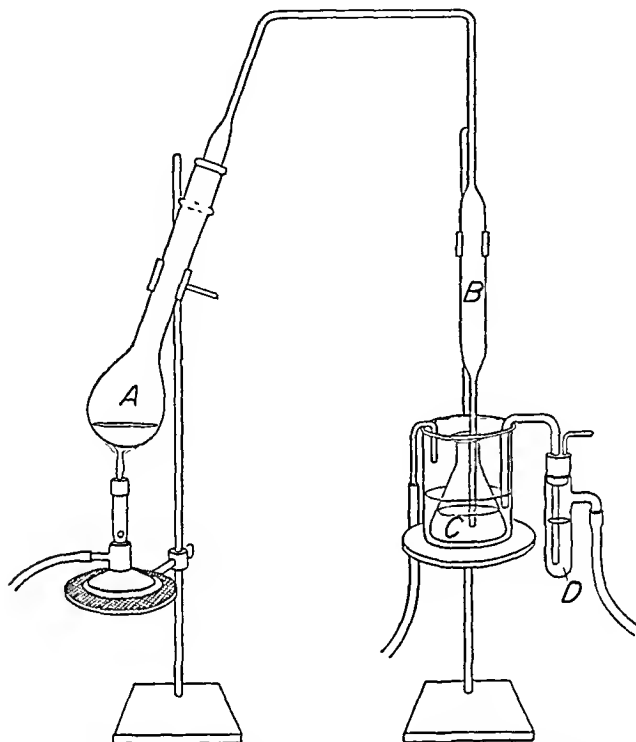


FIG. 42-3. Assembly for Distillation of Arsenic as  $\text{AsCl}_3$ : A, Kjeldahl Flask, 300-ml., or 100-ml.; B, Air Condenser; C, Receiving Flask; D, Constant Level Siphon.

**Methyl Orange Solution.**—Dissolve 0.1 g. of methyl orange in 20 ml. of water plus 1 ml. of 10% NaOH, using heat if necessary. Dilute to 100 ml. and mix. Filter if any sediment is present.

**Procedure.**—(All digestions must be conducted in a fume hood!)

In a 200-ml. casserole place 10 g. of tissue or stomach contents, or 50 ml. of urine. Add 15 ml. of concentrated  $\text{HNO}_3$  and heat on the steam bath with stirring until the evolution of nitrogen oxides ceases and the contents of the casserole have a clear yellow color. It may be necessary to add more  $\text{HNO}_3$  during this process. With urine, the fluid should be evaporated almost to dryness. When the reaction ceases and the casserole contents have a clear, yellow color, slowly add 20 ml. of concentrated  $\text{H}_2\text{SO}_4$ . If the fluid in the casserole turns dark, add more  $\text{HNO}_3$ , about 1 ml. at a time, and continue to heat on the steam bath until the fluid again has a clear, yellow color and does not darken on heating for 5 minutes on the steam bath.

Transfer the contents of the casserole to the Kjeldahl flask washing out the last portion with a little water and adding it to the flask. Add 2 glass beads to the flask. Digest the contents of the Kjeldahl flask over a low flame. When the water and excess  $\text{HNO}_3$  are boiled away the flask contents will probably turn dark. Immediately remove the flame and cautiously add  $\text{HNO}_3$  in portions of about 0.5 ml until the hot contents of the flask have changed to a clear yellow color. Continue the alternate heating and addition of  $\text{HNO}_3$  until the flask contents no longer turn dark when they are heated to the point where fumes of  $\text{SO}_3$  are evolved. Then boil gently for 15 minutes. If further darkening of the flask contents occurs additional 0.5 ml portions of  $\text{HNO}_3$  must be added and the digestion continued until there is no darkening on digesting the flask contents for 15 minutes. The flask contents should now be clear and colorless except for a trace of yellow due to iron.

Allow the flask contents to cool in air for 10 minutes and then hold the flask in running water to cool to room temperature. By means of a pipet slowly add 25 ml of the ammonium oxalate solution shaking the flask during this time. This will cause evolution of nitrogen oxide fumes. Boil the flask contents until all of the water is evolved and fumes of  $\text{SO}_3$  appear. Reduce the flame and boil gently for 15 minutes. Again cool the flask in air for 10 minutes and then in running water. Next introduce 20 ml of water by means of a pipet so that it washes down the mouth and neck of the flask. Mix by shaking and cool in running water to room temperature.

Clamp the air condenser in the position shown in Fig 423. Place in the receiving flask 150 ml of water and support the flask and beaker so that the condenser tube dips about one fourth inch below the surface of the water. Mount the inlet tube and outlet siphon on the beaker. Attach the drain tube of the siphon to a water cock and run in water to fill the siphon and partly fill the beaker pinching the small rubber tube at the top of the siphon. Connect the siphon outlet tube to a convenient drain. Start the water flow into the beaker and adjust the height of the siphon jacket so that the water level in the beaker is about even with the 175 ml mark on the receiving flask but not high enough to float the flask.

Flame the neck of the Kjeldahl flask until its interior is dry and allow it to cool. Add to the Kjeldahl flask 1 g of solid hydrazine sulfate, 50 ml of concentrated  $\text{HCl}$  and 0.5 ml of the  $\text{KBr}$  solution avoiding wetting the ground joint of the flask with the fluids. Mix the flask contents by gentle shaking and at once connect the flask to the air condenser. Seal the ground joint by placing a drop of concentrated  $\text{H}_2\text{SO}_4$  at the top of the joint. Start the distillation using a flame about 2 in. high and continue the distillation until the contents of the receiving flask reach the 175 ml mark. This usually takes about 10 minutes. During the distillation the support holding the beaker should be lowered at intervals so that the air condenser tube never projects more than about one fourth inch below the surface of the fluid in the receiver to avoid serious back suction of the fluid from the receiving flask. When the 175 ml mark is reached quickly lower the beaker and receiving flask and turn off the flame.

Transfer the distillate solution to a 200 ml volumetric flask, add 6 ml of concentrated  $\text{HCl}$  and make up to the mark with water. Take 10 ml of this solution and pass  $\text{H}_2\text{S}$  into it to give a rough idea of amount of arsenic present.

For the titration with  $\text{KBrO}_3$  use one half of the distillate solution unless a distinct yellow color or precipitate resulted from the test with  $\text{H}_2\text{S}$ . In this event

use 50 ml. of the distillate solution. Use a 5-ml. micro-buret for the titration. Warm the fluid to be titrated to about 60° and add one small drop of the methyl orange solution. Run in the bromate solution slowly. When the end point is almost reached, as shown by the partial disappearance of the methyl orange color, add the bromate 1 or 2 drops at a time, waiting 15 seconds between additions. In this way a single drop of the bromate solution will complete the decolorization of the methyl orange. Run a complete blank with distilled water, using approximately the same amount of nitric acid required to oxidize the sample of body material analyzed.

**Calculation.**—Since 1 ml. of the bromate solution oxidizes 0.2 mg. of trivalent arsenic, then:

(ml. of bromate used for the unknown

— ml. of bromate used for the blank)  $\times 0.2 =$  mg. of As (as metal)

in the aliquot titrated. With good reagents, the blank titration should not exceed 0.2 ml. of the bromate solution.

### GUTZEIT METHOD

Analysis by the Gutzeit method of a portion of the distillate solution remaining after the bromate titration serves admirably to check the accuracy of the latter procedure for arsenic.

**Apparatus.** Reaction Bottle.—Use a 2-oz. wide-mouthed glass bottle, fitted with a 1-hole rubber stopper.

**Guard Tube.**—This is a straight calcium chloride-type tube, with the enlarged portion about 16 mm.  $\times$  60 mm.

**Tubes for Gutzeit Papers.**—Obtain glass tubing having an inside diameter of about 2.8 mm. Cut in 120-mm. lengths and flame the ends. Clean, dry, and store in a stoppered test tube.

**Gutzeit Paper Strips.**—Hanford-Pratt sheets of machine-cut strips are excellent. As cut, they are double the length required for an analysis.

**Reagents.** Mercuric Bromide Solution.—Dissolve 10 g. of  $\text{HgBr}_2$  in 200 ml. of 95% ethanol.

**Lead Acetate Solution.**—Dissolve 25 g. of lead acetate in 500 ml. of water and add 1 ml. of glacial acetic acid.

**Copper Sulfate Solution.**—Make up, 5% in water.

**Zinc Metal.**—Baker & Adamson's arsenic-free zinc shot functions well.

**Cotton Impregnated with Lead Acetate.**—Obtain a 6-in. square of good absorbent cotton. Immerse it in the lead acetate solution and squeeze out the excess of liquid. Spread the cotton out flat, peel off thin layers, and tear them into two-inch fluffy pieces. Store these pieces in a rubber-stoppered, wide-mouthed bottle so they will remain moist. This material will keep well.

**Impregnated Gutzeit Strips.**—Cut a Hanford-Pratt sheet in half, crosswise. Take one of the halves and make it into a roll and slip it into a large test tube. Cover it with the  $\text{HgBr}_2$  solution for 30 minutes. Pour the fluid back in the bottle, remove the sheet, and blot lightly between filter papers. Hang for 3 minutes in an oven heated to about 80°C. Cut the strips from the solid portion and store in a cork-stoppered test tube. These impregnated strips will remain active for 6 months,

but their sensitivity decreases with time. For this reason strips from a given batch should be used for both unknown and standards.

**Arsenic Standard**—Weigh out 0.373 g of  $\text{As}_2\text{O}_3$ . Place in a flask and warm with 10 ml of 20%  $\text{NaOH}$  until dissolved. Transfer to a 500 ml volumetric flask and dilute with 400 ml of water. Add 15 ml of concentrated  $\text{HCl}$  make up to 500 ml and mix. One ml contains 1 mg of As (element). Dilute 1:100 for working standard.

**Procedure**—Place in the reaction bottle an aliquot of the distillate solution containing 20 micrograms of arsenic as calculated from the bromate titration. Add sufficient 1:4  $\text{HCl}$  to give a volume of 40 ml and add 2 drops of the  $\text{CuSO}_4$  solution.

Fill the guard tube with cotton moistened with lead acetate solution. Connect one of the narrow glass tubes to the large end of the guard tube by means of a rubber stopper. Push an impregnated strip into the narrow tube and bend a little of the top of the strip so it will slide no further down the glass tube. In the same manner prepare a second Gutzeit generator containing 20 micrograms of As in 40 ml of 1:4  $\text{HCl}$ . Weigh two 15 g portions of the zinc shot. Add one portion of the zinc to a generator bottle and quickly close the mouth with the guard tube Gutzeit strip assembly. Immediately do the same with the other generator. Allow the reaction to proceed for 30 minutes and compare the stains on the two Gutzeit strips. If the bromate titration was correct the length and depth of the orange stains should be the same. If the unknown shows less stain then the analysis should be repeated using a series of standards in the neighborhood of the unknown. From the standard which matches the unknown one can easily calculate the concentration of arsenic in the distillate solution.

## BARBITURATES

For the quantitative procedures use aliquots of Solution B which is made by dissolving Fraction B in ether. The weight of Fraction B is of course the maximum quantity of barbiturate present. Where this fraction weighs more than 20 mg it is frequently almost pure barbiturate.

### MODIFIED METHOD OF KOPPANYI ET AL.<sup>14</sup>

**Reagents** Isopropylamine Solution—Dissolve 5 ml of isopropylamine in 95 ml of absolute methanol. Stored in a refrigerator it keeps quite well.

**Cobaltous Acetate Solution**—Dissolve 0.5 g of  $\text{Co}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot 4\text{H}_2\text{O}$  in 50 ml of absolute methanol. This solution deteriorates after about 2 weeks.

**Procedure**—Transfer to an evaporating dish an aliquot of Solution B representing 0.5 to 2.0 mg of the residue from Fraction B. Evaporate to dryness and dissolve the residue in 1 ml of  $\text{CHCl}_3$ . Pour this solution into a small test tube and rinse the dish with small portions of  $\text{CHCl}_3$  to give a volume of exactly 2 ml in the test tube. Add 0.3 ml of the cobaltous acetate solution and 1.0 ml of the isopropylamine solution shaking the tube after each addition. Compare the OD with that of 2 ml portions of  $\text{CHCl}_3$  containing 0.3 to 1.0 mg of the barbiturate thought to be present treated like the unknown. Read the OD at wavelength 520  $\mu$ . Thiobarbiturates will not give this reaction.

<sup>14</sup> Koppányi, T. Dille, J. M. Murphy, W. S. and Krop, S. J. *Am. Pharmaceut. Assn.* 23, 1074 (1934).

Calculation.—

$$\text{strength of standard} \times \frac{\text{O.D. of unknown}}{\text{O.D. of standard}} = \text{strength of unknown}$$

### DIFFERENTIAL ULTRAVIOLET SPECTROMETRIC METHOD<sup>3,4,5</sup>

The O.D.-wavelength curve for most barbiturates is very different at pH 13.7 (0.5 N NaOH) and at pH 10.3. If a given concentration of a barbiturate is read at 260 m $\mu$ , the O.D. at pH 13.7 will be about four times as great as the O.D. at pH 10.3 and may be used to determine the weight of barbiturate present, as this procedure cancels out the effect of most other extractives. This *differential method* of Goldbaum<sup>15</sup> has proved very valuable in determining microgram quantities of barbiturates in the presence of appreciable amounts of other extractives.

**Reagents.** Sodium Hydroxide, 0.5 N.—This has a pH of about 13.7.

**Ammonium Chloride, Saturated Solution.**—Warm 500 g. of NH<sub>4</sub>Cl with 1 liter of distilled water until solution occurs, and cool. The excess will precipitate on cooling, leaving a permanently saturated solution. When 0.5 ml. of this solution is added to 3 ml. of 0.5 N NaOH a pH of about 10.3 results. This replaces the borate buffer previously used, and was developed by Abernethy and Curphey.<sup>16</sup>

**Procedure.**—Evaporate an aliquot of Solution B representing about 0.1 mg. of barbiturate. Dissolve the residue in 5 ml. of 0.5 N NaOH and read this in the spectrophotometer at wavelength 260 m $\mu$ . To 3 ml. of this solution add 0.5 ml. of saturated NH<sub>4</sub>Cl solution. This gives a pH of about 10.3. Read this solution in the spectrophotometer at wavelength 260 m $\mu$ . Multiply the O.D. of the second reading by 3.5/3.0 and subtract it from the O.D. of the first reading. Compare the difference in O.D. with a *difference curve* obtained by running standards of the barbiturate by the double procedure used for the unknown. Further evidence confirming the identity of the barbiturate is obtained by running the above procedure with the unknown at wavelength intervals of 10 m $\mu$  over the wavelength range of 230 to 280 m $\mu$  and comparing with tables for this differential analysis of various barbiturates.<sup>4,5</sup>

### SEPARATION OF A MIXTURE OF BARBITURATES

In cases of barbiturate poisoning one often encounters a mixture of barbiturates. While some separation can be secured by extraction with the aqueous phase at different pH values, this usually does not effect complete separation. As with alkaloids, the best procedure is to use paper chromatography or paper ionophoresis. The former method is well presented by Curry in a recent publication.<sup>5</sup>

### BORIC ACID

#### METHOD OF SMITH, GOUDIE, AND SILVERTSON<sup>17</sup>

In the presence of about 88% H<sub>2</sub>SO<sub>4</sub>, boric acid gives a red color with carminic acid, and the resulting color is determined photoelectrically.

**Reagents.** Sulfuric Acid, Concentrated, C.P.

<sup>15</sup> Goldbaum, L. R., Anal. Chem., 24, 1605, 1952.

<sup>16</sup> Abernethy, R. J., and Curphey, T. J., Personal communication.

<sup>17</sup> Smith, W. C., Goudie, A. J., and Silvertson, J. N., Anal. Chem., 27, 295, 1955.



**Carminic Acid in Concentrated  $H_2SO_4$ .**—Dissolve 50 mg of carminic acid in about 250 ml of concentrated  $H_2SO_4$  and store in a glass stoppered bottle. Fisher No. A 93 carminic acid is satisfactory.

**Hydrochloric Acid, Approximately 6.0 N**—Mix equal volumes of concentrated HCl and water.

**Lithium Carbonate, Anhydrous, C.P.**

**Boron Standard Stock Solution**—Dissolve 0.2203 g of c.p. crystalline  $Na_2B_4O_7 \cdot 10H_2O$  in water and make up to 250 ml. One ml contains 100 micrograms of boron.

**Procedure**—Place in a platinum crucible or small platinum dish approximately 0.1 g of  $Li_2CO_3$  and add 2 ml of blood or 2 g of tissue. Dry on the steam bath. Place in a muffle furnace, gradually raise the temperature to  $650^\circ C$ , and maintain at this temperature for 90 minutes, or until free from carbon. Cool, and add 2 ml of the 1.1 N HCl solution. Stir to effect solution and pour into a 15 ml conical centrifuge tube. Centrifuge until clear.

Transfer 1 ml to a 20 x 150 mm boron free test tube. Add 5 ml of concentrated  $H_2SO_4$  and 5 ml of the carminic acid solution. Mix with a glass rod ending in a 15 mm ring at right angle to the rod. Cover the mouth of the tube with a small watch glass and allow to stand for 5 minutes. Read in a photoelectric colorimeter set at wavelength 575 m $\mu$ . Compare the optical density with the O.D. curve obtained by running the entire procedure with 2 ml portions of water containing 5 to 30 micrograms of boron.

## CARBON MONOXIDE

### MODIFIED METHOD OF CHRISTMAN AND RANDALL<sup>18</sup>

The blood is introduced into an evacuated bottle laked with water, and treated with acid ferricyanide. This forms brown methemoglobin and liberates CO and  $O_2$  from combination with hemoglobin. The evolved gases are transferred to an evacuated receiver containing standard  $PdCl_2$  solution. The resulting reaction is  $CO + PdCl_2 + H_2O = CO_2 + Pd + 2HCl$ . The weight of metallic Pd formed is determined by analyzing the  $PdCl_2$  solution before, and after, the reaction.

**Apparatus (Fig. 424).** **Reaction Bottle**—A 4 oz wide mouthed bottle (1) is provided with a well fitting 2 hole rubber stopper. One hole of the stopper carries an inlet tube of 2 mm bore capillary glass extending almost to the bottom of the bottle and having an 8 ml reservoir (2) and a capillary bore, stopcock (3) at the top. The second hole carries an ell of capillary glass tubing with a bore of about 2 mm. The vertical part of the ell should not project below the bottom of the stopper.

**Receiving Chamber**—This is a pear shaped glass bulb of about 30 ml capacity (4). To its upper end is sealed a short piece of 2 mm bore capillary tubing ending in a 2 way capillary bore stopcock (5). One hole of the stopcock communicates with a vertical, 6 ml reservoir (6) and the other with a glass ell of 2 mm bore capillary tubing. A straight glass stopcock (7) is sealed to the lower end of the chamber.

**Rotating Cylinder**—This is a metal cylinder (8) about 4 in long, with an inside diameter of about 2 in. Three pieces of flat spring are soldered to the outside of the cylinder wall. These springs have curved ends projecting inside the cylinder.

<sup>18</sup> Christman, A. A. and Randall, E. L., J. Biol. Chem., 102, 595, 1933.

through slots in its wall. The springs hold the reaction bottle firmly when placed in the cylinder. The cylinder is mounted coaxially to the end of a shaft, which rotates in two supporting bearings. A pulley on the shaft connects by a belt to the pulley of a gear from a small motor.

**Support for Rotating Receiving Chamber.**—A wooden strip about 5 in. long is screwed to the metal bracket of a funnel support. Short, vertical pieces of wood

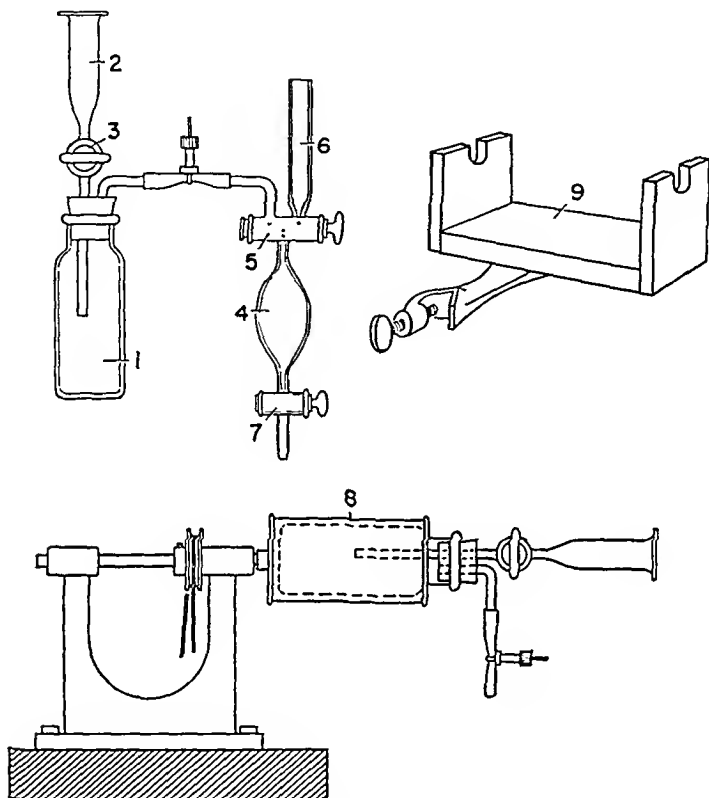


FIG. 42-4. Apparatus for Determining Carbon Monoxide in Blood: 1, Reaction Bottle; 2, Reservoir; 3, Stopcock; 4, Receiving Chamber; 5, 2-way Stopcock; 6, Reservoir; 7, Stopcock for Draining Receiving Chamber; 8, Rotating Metal Cylinder, Holding Reaction Bottle; 9, Support for Rotating Receiving Chamber.

are nailed to the ends of the wooden strip. A slot, with rounded bottom, is cut in each of the vertical pieces. The receiving chamber (4) may be supported horizontally in these two slots, and is rotated by connecting its exit tube (7) through a short piece of rubber tubing to a slow-moving, horizontal shaft turned by a geared-down motor.

**Reagents. Ferricyanide Solution, 32%.—**Dissolve 16 g. of  $K_3Fe(CN)_6$  in water and make up to 50 ml. It keeps well.

**Lactic Acid, Sp. Gr. 1.2.**

**Acid Ferricyanide Solution.**—Mix 5 ml. of the 32% ferricyanide solution with 0.43 ml. of the lactic acid. Make up as used.

**Octyl Alcohol**

**Standard Palladium Chloride Solution**—Warm 100 mg of c.p.  $\text{PdCl}_2$  with 30 ml of water plus 0.5 ml of concentrated  $\text{HCl}$ . When solution is complete dilute to 100 ml in a volumetric flask. It keeps well in a glass stoppered bottle.

**Aluminum Sulfate Solution**—Dissolve 2 g of  $\text{Al}(\text{SO}_4)_3 \cdot 9\text{H}_2\text{O}$  in 20 ml of water.

**Potassium Iodide Solution**—Dissolve 2 g of  $\text{KI}$  in 12 ml of water. Prepare just before use.

**Procedure**—Moisten the rubber stopper with a little water and press it firmly into the neck of reaction bottle (1). Connect to the glass ell a short piece of pressure tubing provided with a screw pinch clamp. Evacuate the bottle with a good pump and close the pinch clamp. Place 2 drops of octyl alcohol in reservoir (2) and admit the fluid into the bore of stopcock (3). Place 4 ml of water in reservoir (2). Select a good 2 ml Ostwald pipet with moderately thick tip and cover the tip with a sleeve of rubber tubing about three eighths inch long. Shake the blood bottle to uniformly suspend the red cells and fill the pipet with the blood. Insert the tip of the pipet into the reservoir (2) until the rubber sleeve makes a tight joint with the bottom of the reservoir. Carefully open stopcock (3) and draw the blood into the bottle avoiding any entrance of air. Refill the pipet with water from reservoir (2) and draw this into the bottle. Rinse the pipet a second time with the reservoir water and remove the pipet. Drain the reservoir fluid into the bottle and use a little water to wash all traces of blood into the bottle. Gently shake the bottle to take the blood. Place in reservoir (2) 0.3 ml of the acid ferricyanide and 1 ml of water and mix with a glass rod. Slowly admit this solution into the bottle while gently shaking the laked blood. Use two 1 ml portions of water to wash all of the ferricyanide into the bottle.

Place a small block of wood under the base of the cylinder support (8) to keep the open end of the cylinder a little above the horizontal plane. Insert reaction bottle (1) into the metal cylinder. Take care to avoid any entrance of the fluid into the glass ell of the reaction bottle during this part of the operation. Connect shaft pulley and drive pulley with the belt and slowly rotate the reaction bottle for 15 minutes.

Near the end of the period for rotating bottle (1) partly evacuate the receiving chamber (4) and clamp it in a vertical position. Using a good Ostwald pipet transfer 3 ml of the  $\text{PdCl}_2$  solution to reservoir (6) and admit this solution into the chamber. Rinse every trace of the  $\text{PdCl}_2$  solution into the chamber using two 2 ml portions of water for this purpose. Again connect the glass ell to the pump and evacuate well being careful to avoid loss of any fluid by foaming.

Connect reaction bottle (1) and receiving chamber (4) by means of the closed rubber sleeve as shown in Fig. 424. Open stopcock (5) to connect with the ell and unscrew the pinch clamp. Make sure that the lumen of the rubber tube is open. Through reservoir (2) admit mercury into bottle (1) until all of the rarefied gas in the bottle passes into chamber (4). At intervals during this procedure slightly loosen the clamp holding chamber (4) and gently shake its contents. Near the end of this gas transfer slant the bottom of bottle (1) somewhat toward chamber (4) so as to leave no gas trapped at the top of the bottle. When the fluid in the bottle begins to enter the horizontal part of the glass ell turn off stopcocks (5) and (3). Then cautiously open stopcock (5) until the fluid reaches its bore. See that no trace of fluid from the reaction bottle enters chamber (4) as this may reduce some of the  $\text{PdCl}_2$ .

Disconnect the rubber tube from the receiving chamber (4), and admit enough water through the reservoir (6) to fill the capillary neck of (4). Place the receiving chamber (4) in a horizontal position on the wooden support and connect the tube from the 1-way stopcock to the gear shaft from the motor by means of a short piece of rubber tubing. Slowly rotate the receiving chamber for 10 minutes. If CO is present in the gas of the receiving chamber, the  $\text{PdCl}_2$  solution will darken, and metallic palladium will precipitate. At the end of the rotation period, clamp receiving chamber (4) in a vertical position. Place 0.2 ml. of the aluminum sulfate solution in reservoir (6) and admit it into the chamber, followed by a few drops of water and shake the fluid in (4). This should complete the separation of metallic palladium. When this occurs, filter the chamber contents into a 50-ml. volumetric flask, through a small filter paper. When all the fluid has drained from chamber (4), close stopcock (7) and evacuate the chamber somewhat by suction through its glass ell, and close stopcock (5). Fill the reservoir with water and admit this into the chamber. Pass the wash water through the filter, using it to wash the sides of the filter. Repeat the rinsing of the chamber and subsequent washing of the filter paper. Finally, wash the filter paper with two additional small portions of water. The volume of fluid in the flask should now be 25 to 30 ml.

In a second flask, place 2 ml. of the standard  $\text{PdCl}_2$  solution and add water until the volume equals that in the first flask. To each flask add 5 ml. of the KI solution and mix. Make up to 50 ml. and again mix. Using a photoelectric colorimeter set at wavelength 408  $m\mu$ , determine the optical density of the standard and unknown.

Calculation.—

$$3 - \left( 2 \times \frac{\text{O.D. of unknown}}{\text{O.D. of standard}} \right) = \text{mg. of PdCl}_2$$

used to oxidize the CO. This figure  $\times 4.705$  = Grams of CO-Hemoglobin per 100 ml. of the blood.

One should also determine the total hemoglobin content of the blood, using the acid hematin method. From this result, one can calculate the fraction of the total hemoglobin which was present as CO-Hemoglobin. In fatal cases of CO poisoning, the CO-Hemoglobin usually constitutes 60 to 75% of the total hemoglobin.

## CYANIDE

### LIEBIG METHOD

(See p. 2111 of this work)

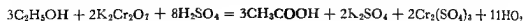
*Procedure.*—Measure a large aliquot (at least 0.5) of the distillate from tissues or stomach contents, and add 3 ml. of 10% NaOH. Titrate with 0.1 N  $\text{AgNO}_3$  until a faint, permanent turbidity develops. The reaction is:  $2\text{NaCN} + \text{AgNO}_3 = \text{NaAg(CN)}_2 + \text{NaNO}_3$ . The  $\text{NaAg(CN)}_2$  is soluble, but the first drop of excess  $\text{AgNO}_3$  produces insoluble  $\text{AgCN}$ .

Calculation.—Each ml. of 0.1  $\text{AgNO}_3$  used is equivalent to 9.8 mg. of NaCN or 13.0 mg. of KCN.

## ETHANOL

DICHROMATE TITRATION METHOD OF HARGER<sup>19</sup>

The ethanol is first separated by distillation and the distillate used for the analysis. In the presence of hot approximately 17 N  $\text{H}_2\text{SO}_4$  ethanol and dichromate react as follows



Excess standard dichromate is employed and the remaining dichromate is titrated with a solution of ferrous sulfate and methyl orange until a permanent red color is reached. Consumption of 1 mg of potassium dichromate requires 0.235 mg of ethanol.

**Apparatus** Distilling Flask Conventional type 125 ml with the side arm cut off to about 2 inches

Condenser—Liebig type with 10-in jacket. Use vertically to facilitate rinsing the inner tube. The latter made of thin 8 mm glass has a 2 in ell at the top parallel with the arm of the distilling flask and protrudes about 4 in below the bottom of the jacket.

Receiving Tube— $1\frac{1}{2} \times 200$  mm Lewis Benedict sugar tube graduated at 125 and 250 ml is satisfactory.

Buret This is 5 ml micro type graduated in 0.02 ml and with the tip drawn out to a rather fine point. About 1 in above the zero mark blow a small bulb ending in a U tube for suction filling.

**Reagents** Store all reagents in glass stoppered bottles.

Sodium Tungstate 10%

Sulfuric Acid 0.67 N—Dissolve 10 ml of concentrated  $\text{H}_2\text{SO}_4$  in 500 ml of water. Titrate and adjust strength if necessary.

Sulfuric Acid Concentrated C P—This should give very little blank in the analysis.

Sulfuric Acid Solution 1:1—Slowly add 250 ml of concentrated  $\text{H}_2\text{SO}_4$  to 250 ml of water shaking and cooling during the addition.

Standard Dichromate Solution 0.0434 N—Dissolve 2.129 g of dry C P  $\text{K}_2\text{Cr}_2\text{O}_7$  in water and make up to 1 liter. It keeps indefinitely. One ml is equivalent to 0.5 mg of ethanol.

Ferrous Iron Solution Dissolve 50 g of crystalline ferrous sulfate in 150 ml of water. Add 30 ml of concentrated  $\text{H}_2\text{SO}_4$  and make up to 250 ml. It keeps quite well.

Methyl Orange Solution 0.1%—See Ramberg Sjoström method p. 2126.

Red Titration Fluid—Mix 35 ml of the 1:1  $\text{H}_2\text{SO}_4$  with 15 ml of the methyl orange solution and add 1 ml of the ferrous iron solution. Mix and cool. Kept in a refrigerator this solution will retain its strength for several days.

**Procedure** Distillation of Body Materials **Tissues**—These are steam distilled as described on page 2110.

**Blood**—In the 125 ml distilling flask place 20 ml of water. Add 1 ml of blood and rinse the Ostwald pipet with the fluid in the flask. Add 2 ml of the sodium

<sup>19</sup> Harger R. N. J. Lab. Clin. Med. 20, 746 1935.

<sup>20</sup> Harger R. N. Raney B. B. Bridwell E. G. and Kitchel M. F. J. Biol. Chem. 183 197 1950.

tungstate solution and, while shaking the flask, add 2 ml of the 0.67 *N* H<sub>2</sub>SO<sub>4</sub>. Put 2 glass beads in the flask, close with a well washed rubber stopper, connect to the condenser, and put the receiving tube in place. Heat with a micro burner and distill over 10 to 12 ml. Disconnect the flask and rinse the condenser tube twice with about 2 ml of water from a wash bottle. Dilute distillate and washings to 25 ml and mix. If the blood alcohol level is below 0.1%, the distillate should be made up to 12.5 ml.

*Urine*.—Use 1 ml of urine plus 25 ml of water, but no tungstate or acid. Then proceed as with blood.

*Oxidation of Distillate*.—Place in a 19 x 150 mm test tube an aliquot of the distillate representing 0.2 to 0.4 ml of blood or urine, or 0.2 to 0.5 g of tissue. Add water, if necessary, to give a volume of 5 ml. Next add 1 ml of the standard dichromate and mix. Using a pipet with a rather large opening at the tip, add 5 ml of concentrated H<sub>2</sub>SO<sub>4</sub>. Mix with a glass rod ending in a 15 mm ring at right angle with the rod. This raises the fluid temperature to slightly above 100°C so no further heating is necessary. Run a blank with 5 ml of water, but use only 0.2 ml of the dichromate solution. Allow the tubes to stand in the rack for 10 minutes, and then place in cold water for 5 minutes.

*Titration of Remaining Dichromate*.—Clamp the reaction tube just below the buret tip. Place in the reaction tube a 4 mm glass tube with a U bend at the top so that it will hang on one side of the reaction tube and extend almost to the bottom. Through this tube bubble a slow current of air which is purified by passing through activated charcoal. Titrate to the first permanent red color. The beginning titration rate should be 2 to 3 drops per second, but near the end point it should be reduced to a drop every 2 seconds. The end point is sharp. After titrating the blank, add a second 0.2 ml of the dichromate and re titrate. Finally, add 1 ml of the dichromate to the blank tube and again titrate.

*Calculations*.—Designate the titration figures as follows: *U* = unknown, *a* = blank, *b* = titrated blank plus 0.2 ml dichromate, *D* = extra 1 ml of dichromate. Then,

$$\frac{U - (b - a)}{D} \times 0.5 = \text{Mg}$$

ethanol in the aliquot analyzed. To calculate mg of ethanol per ml. of blood or urine, or per g of tissue, multiply the above result by 1 over the fraction of these quantities represented by the aliquot analyzed. For best results the aliquot analyzed should reduce 60 to 90% of the dichromate. If titration *U* consumes only one or two drops of the red fluid, repeat the analysis with a smaller volume of the distillate. Blood from non alcoholic subjects yields a small blank by the method, which averages about 0.08 mg of ethanol per ml of blood. In practice we subtract 0.10 mg for the blank.

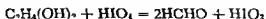
NOTE.—Numerous variants of the dichromate method for ethanol have been published. For reviews of many of these see Friedemann and Dubowski<sup>21</sup> and Haeger.<sup>5</sup> In a number of the methods the residual dichromate is determined photoelectrically, using wavelength 450 mμ.

<sup>21</sup> Friedemann, T. E., and Dubowski, K. M., Chapter V in *Manual of Chemical Tests for Intoxication*, Ed by Committee on Medicolegal Problems, Am Med Assn, Chicago, Am Med Assn, 1959.

## ETHYLENE GLYCOL

METHOD OF HARGER AND FORNEY<sup>22</sup>

Ethylene glycol reacts with periodic acid to form formaldehyde and iodic acid



Thus each atom of oxygen used yields two molecules of formaldehyde. Other glycols react with periodic acid but form one molecule or less of formaldehyde per atom of oxygen used.

**Reagents** Sulfuric Acid 0.67 N—See section on Ethanol above

Sodium Tungstate, 10%

Periodic Acid 0.1 M—Dissolve 2.13 g of  $\text{NaIO}_4$  in 100 ml of 0.33 N  $\text{H}_2\text{SO}_4$

Schiff Elvove Reagent—See section on formaldehyde p. 2112

**Procedure** Blood—Take 3 ml of blood with 21 ml of water and add 3 ml of the sodium tungstate solution. With vigorous shaking add dropwise 3 ml of 0.67 N  $\text{H}_2\text{SO}_4$ . Stopper the flask, shake well and filter. The filtrate should be clear and free from protein.

Place in a small test tube 1 ml of the protein free filtrate and add 4 ml of water followed by 0.25 ml of the periodic acid. Shake to mix. Allow to stand for 10 minutes, quickly add 2 ml of the Schiff Elvove reagent and mix. After 25 minutes read with a photoelectric colorimeter set at wavelength 555  $\mu$ . Compare the result with the optical density curve for 5 ml of water containing 10 to 0 micrograms of ethylene glycol and run in the same way. If the color of the unknown is considerably deeper than that of the 70 microgram standard, repeat the analysis with less of the protein free filtrate.

Normal blood gives a small blank. In about 98% of cases it is equivalent to between 0.01 and 0.16 mg of ethylene glycol per ml of blood. About 2% of normal bloods give a blank equivalent to 0.17 to 0.35 mg of ethylene glycol per ml of blood. Even the highest blank is only about one tenth of the blood glycol concentration found in rapidly fatal cases of ethylene glycol poisoning.

**Urine**—Dilute the urine 20 fold or more and proceed as with the protein free filtrate of blood. Normal urine gives a higher blank than that of blood but in glycol poisoning the urine level of glycol is 2 or 3 times that of blood.

**Tissues**—Using a small blender homogenize 5 g of tissue with 25 ml of water. Transfer to a flask and wash out the blender jar with two 5 ml portions of water adding the washings to the flask. Next add 5 ml of sodium tungstate solution and with shaking 5 ml of the 0.67 N  $\text{H}_2\text{SO}_4$ . Filter and proceed as with the protein free filtrate of blood. Normal tissues give a somewhat higher blank than does normal blood but in glycol poisoning the tissue concentration is higher than that of blood.

MODIFIED METHOD OF LEHMAN AND NEWMAN<sup>23</sup>

In this method the residual periodic acid is reduced with an excess of standard arsenious acid and the remaining arsenious acid is titrated with 0.1 N iodine solution.

**Reagents** Periodic Acid, 0.1 M—See Method of Harger and Forney above

<sup>22</sup> Harger R. V. and Forney R. B. J. Forensic Sciences 4, 136 1959

<sup>23</sup> Lehman A. J. and Newman H. W. J. Pharmacol. Exptl. Therap. 60, 312 1937

**Arsenious Acid, 0.1 N.**—Dissolve 4.95 g. of C.P.  $\text{As}_2\text{O}_3$  in 150 ml. of water plus 15 g. of anhydrous  $\text{Na}_2\text{CO}_3$ . Make acid by adding 25 ml. of 5%  $\text{H}_2\text{SO}_4$ , and dilute to 1 liter.

**Sodium Bicarbonate, 8%.**

**Standard Iodine Solution, 0.1 N.**—Prepare as usual in 1.8% KI. Each ml. is equivalent to 3.1 mg. of ethylene glycol.

**Potassium Iodide.**—Dissolve 1 g. of KI in 5 ml. of water.

**Procedure.**—In a flask place 15 ml. of the protein-free filtrate from blood or tissues, or 15 ml. of diluted urine. Add 25 ml. of water and 5 ml. of the  $\text{HIO}_4$  solution. Place the flask in cold water and allow to stand for 15 minutes. Add 10 ml. of the  $\text{NaHCO}_3$  solution, followed by exactly 15 ml. of the standard  $\text{As}_2\text{O}_3$  solution. Let stand at room temperature for 15 minutes. Add 1 ml. of 1% starch solution and titrate with the 0.1 N iodine solution. Run a blank with water substituted for the protein-free filtrate or diluted urine.

**Calculation.**—(ml. of 0.1 N iodine used for unknown — ml. of 0.1 iodine used for blank)  $\times$  3.1 = mg. of ethylene glycol present in the aliquot analyzed. Multiply this result by 1/fraction of 1 ml. of blood or urine, or g. of tissue, represented by the aliquot used in the analysis.

Compare the result with that obtained in the Harger and Forney method, above. If they agree, the result almost certainly represents ethylene glycol.

**NOTE.**—Results by the two methods are also identical for ethanolamines, but such amines are very unlikely in body materials and periodic acid oxidation of them produces ammonia, which can be determined by distilling the titrated fluid after making it alkaline.

## ISOPROPYL ALCOHOL AND ACETONE

### PERSULFATE METHOD OF GINTHER AND FINCH <sup>24</sup>

In isopropyl alcohol poisoning much of the alcohol is converted to acetone, so one always finds both compounds in such cases. In the modified procedure of Ginther and Finch one determines the acetone by reaction with salicylaldehyde before, and after, converting the isopropyl alcohol to acetone by means of persulfate.

**Reagents.** Potassium Persulfate, 1%.

Sodium Bisulfite, 5%.

Sodium Hydroxide, 40%, W/V.

**Salicylaldehyde Solution, 20%.**—Dissolve 5 ml. of salicylaldehyde in 20 ml. of 95% ethanol.

**Acetone Standard.**—Dissolve 1.26 ml. of acetone in water and dilute to 1 liter which is 1.0 mg. of acetone per ml. Dilute properly for working standards.

**Isopropyl Alcohol Standard.**—Dissolve 1.27 ml. of pure isopropyl alcohol in water and dilute to 100 ml. For working standard, dilute 50-fold, giving 0.2 mg. per ml.

**Procedure.**—Analyze the distillates from body materials made as described under Ethanol, above.

**Free Acetone.**—In a 25-ml. glass-stoppered volumetric flask place an aliquot of the distillate representing 0.2 ml. of blood or urine, or 0.2 g. of the tissue, and dilute to 5 ml. In a second flask place 0.4 mg. of acetone in 5 ml. of water, and in a third flask place 5 ml. of water. To each flask add 4 ml. of 40% NaOH and

<sup>24</sup> Ginther, G. B. and Finch, R. C., *Anal. Chem.*, **32**, 1894, 1960.



1 ml of 20% salicylaldehyde solution Shake immediately to avoid precipitation Stopper the flasks and heat them in a water bath at 80°C for 15 minutes Cool and dilute to the 25 ml mark and mix Dilute suitably and determine the optical density at wavelength 500 m $\mu$  setting the blank at 100% transmittance If the orange color of the unknown is very far from that of the standard use less or more of the distillate Employ the OD formula given below to calculate the acetone content of the unknown

**Acetone from Isopropyl Alcohol Plus Free Acetone**—In a 25 ml flask place the same aliquot of distillate as was used for free acetone In a second flask place 0.4 mg of isopropyl alcohol Dilute both to 5 ml In a third flask place 5 ml of water To each add 1 ml of 1% potassium persulfate Mix stopper and place in a water bath at about 80°C for 15 minutes Cool add 1 ml of 5% sodium bisulfite and mix Next add 4 ml of 40% NaOH and 1 ml of the salicylaldehyde solution and again mix Heat at 80°C for 15 minutes and cool Make to volume dilute suitably and read at wavelength 500 m $\mu$  with the blank set at 100% transmittance

**Calculation**—

$$\text{strength of standard} \times \frac{\text{OD of unknown}}{\text{OD of standard}}$$

= strength of unknown expressed as isopropyl alcohol

Subtract from this the free acetone determined above expressed as isopropyl alcohol (mg acetone  $\times$  1.03) The difference is the isopropyl alcohol Use the dilution factor to calculate the concentration of free acetone and isopropyl alcohol in the body material analyzed

## LEAD

**Reagents**—Most of the chemicals used are now available in practically lead-free condition Only the sodium citrate requires deleading Use double-distilled water the final distillation being from Pyrex glassware

**Sulfuric Acid Concentrated, C P**

**Nitric Acid Concentrated C P**

**Dilute Nitric Acid**—Dissolve 1 ml of concentrated HNO<sub>3</sub> in 100 ml of water

**Ammonium Hydroxide Concentrated, C P**

**Cyanide Solution**—Use a freshly prepared 10% solution of C P KCN

**Perchloric Acid 60%**

**Hydroxylamine Solution**—Dissolve 20 g of NH OH HCl in water and dilute to 100 ml

**Sodium Citrate Solution**—Dissolve 50 g of C P sodium citrate in water and make up to 1 liter Shake in a large separatory funnel with 10 ml of dithizone Solution I below After separation draw off the CHCl<sub>3</sub> layer Repeat this procedure until the CHCl<sub>3</sub> layer retains its original green color Remove dithizone dissolved in the aqueous solution by repeated extraction with CHCl<sub>3</sub> only

**Dithizone Solutions**—Weigh out 10 mg of diphenylthiocarbazone and dissolve in 50 ml of CHCl<sub>3</sub> This contains 20 mg % Wt Vol

**Solution I**—To 6 ml of the 20 mg % dithizone solution add 34 ml of CHCl<sub>3</sub> to give 3 mg %

*Solution II.*—To 3 ml. of the 20 mg. % solution add 57 ml. of  $\text{CHCl}_3$ , to give 1 mg. %.

*Standard Lead Solution.*—Dissolve 0.1598 g. of C.P.  $\text{Pb}(\text{NO}_3)_2$  in water, add 1 ml. of concentrated  $\text{HNO}_3$  and make up to 100 ml. with water. This contains 1 mg. of Pb per ml. For working standards dilute this stock solution 100-fold, or more, with the dilute  $\text{HNO}_3$ .

*Procedure.*—For satisfactory results, use: 100 ml. of urine; 10 ml. of blood; 10 g. of tissue, homogenized with 30 ml. of water; or 5 g. of bone.

Place the sample in a 500-ml. Pyrex Kjeldahl flask. Add 5 ml. of concentrated  $\text{H}_2\text{SO}_4$  and two glass beads. Heat over a small flame until most of the water has distilled off, and the fluid begins to char and spatter slightly. Cool 2 minutes, add 2 ml. of concentrated  $\text{HNO}_3$  and boil until brown fumes cease to be evolved. If the fluid darkens, cool 2 minutes, add 2 ml. of concentrated  $\text{HNO}_3$ , and boil as before. Continue this treatment until the fluid does not char on boiling after evolution of brown fumes ceases. Cool, and add 1 ml. of concentrated  $\text{HNO}_3$  and 1 ml. of perchloric acid. Boil until most of the perchloric acid is volatilized. Cool. If the solution is still yellow, add 0.5 ml. of the  $\text{HNO}_3$  and 0.5 ml. of the perchloric acid and boil again until the perchloric acid is mostly distilled off. The final fluid, on cooling, should be water-clear.

To the fluid in the flask add 25 ml. of water and 10 ml. of the citrate solution, and mix. If necessary, warm until any solid material is dissolved. Cool, and add 1 ml. of the hydroxylamine solution and 1 drop of phenol red indicator. Using a buret, add the concentrated  $\text{NH}_4\text{OH}$  until a pH of about 8.0 is reached. The color change is pink, through yellow, to pink.

Quickly transfer the flask contents to a 125-ml. Pyrex Squibb separatory funnel containing 5 ml. of the KCN solution. Rinse the flask with a little water and add this to the funnel. Add 3 ml. of dithizone Solution I, stopper the funnel, and shake the contents vigorously for 1.5 minutes. Transfer the  $\text{CHCl}_3$  layer to a second separatory funnel and extract the aqueous fluid with another 3 ml. of dithizone Solution I. Add this to the first dithizone extract and continue the extraction procedure until the last  $\text{CHCl}_3$  layer has only its original green color. To remove the lead from the dithizone complex, add 50 ml. of the dilute  $\text{HNO}_3$  to the combined dithizone extracts and shake vigorously for 1 minute. If bismuth is present, the dithizone will not all return to its original green color, but will be yellow-green. To remove any traces of the bismuth complex from the  $\text{HNO}_3$  solution, add to this solution 5 ml. of  $\text{CHCl}_3$  only, and shake. Discard the  $\text{CHCl}_3$  extracts.

To the acid solution add 10 ml. of the citrate solution, 1 ml. of the hydroxylamine solution and 1 drop of phenol red indicator, and adjust to pH 8.0 with concentrated  $\text{NH}_4\text{OH}$ . Add 5 ml. of the cyanide solution and 25 ml. of dithizone Solution II. Shake for 1 minute. Pass the  $\text{CHCl}_3$  layer through a small, dry Whatman No. 1 filter paper and collect in a 50-ml. glass-stoppered cylinder.

Read the O.D. of the final dithizone extract with a photoelectric colorimeter set at wavelength 510 m $\mu$ , using  $\text{CHCl}_3$  only for the 100% transmittance setting. Calculate the weight of Pb in the dithizone extract by comparing its O.D. with the O.D. curve of 50-ml. portions of the dilute  $\text{HNO}_3$  containing 1 to 20 micrograms of Pb and carried through the procedure described in the preceding paragraph.

Conduct a blank analysis, substituting 50 ml. of water for the unknown sample and employing the same procedure and quantities of all reagents used for the unknown. Subtract the blank from the unknown.

Thallium also forms a red complex with dithizone and would be recorded as lead in the method just described. Although the presence of thallium in body materials is very unlikely, this possibility can be easily tested because thallic chloride is soluble in ether while lead chloride is not.<sup>25</sup> For such a check test see Thallium below, page 2145.

## MERCURY

### METHOD OF LAUG AND NELSON,<sup>26</sup> MODIFIED BY YUNGHANS<sup>27</sup>

**Reagents** Mercury Standard—Weigh exactly 0.5 g of mercury dissolve in 10 ml of concentrated  $\text{HNO}_3$  and dilute with water to 100 ml. To 1 ml of this stock solution add 10 ml of concentrated  $\text{HNO}_3$  and dilute to 1 liter with water. One ml of this working standard contains 5 micrograms of Hg.

Sulfuric Acid Approximately 18 N. To 200 ml of distilled water add an equal volume of C.P. concentrated  $\text{H}_2\text{SO}_4$ . Mix and cool.

Acetic Acid Approximately 6 N. Dilute 30 ml of glacial acetic acid to 100 ml with water.

Ammonium Hydroxide, Approximately 9 N. Dilute 600 ml of concentrated  $\text{NH}_4\text{OH}$  with water to give a volume of 1 liter.

Hydroxylamine Solution—Dissolve 50 g of  $\text{NH}_2\text{OH} \cdot \text{HCl}$  in 100 ml of water.

Dithizone Solution—Weigh out 10 mg of diphenylthiocarbazone and dissolve in 100 ml of  $\text{CHCl}_3$ . For extraction of Hg dilute this stock solution ten fold with  $\text{CHCl}_3$ .

Permanganate—Use C.P.  $\text{KMnO}_4$  finely powdered.

**Procedure**—Suitable samples for analysis are urine 100 ml, blood 10 ml and tissues 10 g homogenized with 30 ml of water. Place the sample in a 250 ml Erlenmeyer Pyrex flask with standard taper mouth. Add 10 ml of the 18 N  $\text{H}_2\text{SO}_4$  and approximately 0.5 g of the  $\text{KMnO}_4$ . Connect the flask to a 15 in Liebig condenser with standard taper joint and reflux with gentle boiling. When the purple color disappears add about 0.2 g of the  $\text{KMnO}_4$  through the condenser tube. Continue the boiling and addition of  $\text{KMnO}_4$  until a total of about 1.5 g of  $\text{KMnO}_4$  has been used. Wash down the condenser tube with a little water and boil for 5 minutes. Cool and add the  $\text{NH}_4\text{OH} \cdot \text{HCl}$  solution dropwise until the permanganate color is discharged and add 1 ml in excess. Add 2 ml of the 6 N acetic acid.

Immediately transfer the fluid in the flask to a 250 ml Squibb separatory funnel and make up to 180 ml with rinsings from the flask. Add 10 ml of the diluted dithizone solution and shake for about 2 minutes. Transfer the chloroform layer to a second separatory funnel containing 25 ml of the ammonia solution. Pass the chloroform layer through a small dry filter paper and read in a photoelectric colorimeter set at wavelength 476 m $\mu$  using chloroform for the 100% transmittance setting.

**Standards**—Prepare a series of standards by adding 0.5 to 4.0 ml of the dilute Hg standard to 10 ml of 18 N  $\text{H}_2\text{SO}_4$ , 1 ml of  $\text{NH}_4\text{OH} \cdot \text{HCl}$  solution and 2 ml of 6 N acetic acid. Dilute to 180 ml, shake with 10 ml of the dilute dithizone

<sup>25</sup> Shaw P. A. J. Ind. Eng. Chem. Anal. Ed. 5, 93, 1933.

<sup>26</sup> Laug E. P. and Nelson K. W. J. Assn. Off. Agr. Chemists 25, 399, 1942.

<sup>27</sup> Yungmans R. Personal communication.

solution, and proceed as with the unknown. Use the O.D. curve of the standards to calculate the weight of Hg in the dithizone extract from the unknown.

**Blank.**—Conduct a reagent blank analysis, substituting 50 ml. of distilled water for the sample analyzed. Subtract the blank result from the unknown.

## METHANOL

### DICHROMATE METHOD <sup>19</sup>

If methanol is the only reducing substance present in the distillate from body materials it may be determined by the dichromate titration method described above for ethanol. Since dichromate oxidizes methanol quantitatively to  $\text{CO}_2$  and  $\text{H}_2\text{O}$ , 1 ml. of the 0.0434 *N* dichromate is equivalent to 0.232 mg. of methanol. Thus, one uses the formula for ethanol, but substitutes 0.232 for 0.5.

### MODIFIED WRIGHT-ELVOVE METHOD <sup>28</sup>

In addition to determining the concentration of methanol in the distillate, this method also serves to check the dichromate result for methanol. The reason for adding ethanol is explained on p. 2113.

**Reagents.** Standard Methanol Solution, 1%, W/V.—Dissolve 1.26 ml. of absolute methanol in water, dilute to 100 ml. in a volumetric flask, and mix. This keeps indefinitely. For preparing working standards, dilute 50-fold with water to give 0.2 mg. per ml.

**Other Solutions.**—Use those listed for the Wright-Elvove qualitative test for methanol, described on p. 2113.

**Procedure.**—Transfer to a small test tube an aliquot of the distillate containing 0.4 mg. of methanol as calculated from the dichromate analysis, assuming that only methanol was present. Make this up to a volume of 2 ml. In a second tube place 2 ml. of diluted standard containing 0.2 mg. of methanol per ml. From this point follow the procedure given for the Wright-Elvove qualitative analysis described on p. 2113. When development of color has continued for 30 minutes, determine the optical density of the standard and unknown when examined at wavelength 555  $\text{m}\mu$ . If they are the same, the distillate contained only methanol and the concentration calculated from the dichromate titration is correct. If the unknown color is weaker than that of the standard, repeat the analysis, using a series of standards containing from 0.1 to 0.2 mg. of methanol per ml., and a larger aliquot of the distillate, if necessary. Compare with the standard which most nearly matches the unknown, since the color deviates somewhat from Beer's Law.

## PHENOL

### PRECIPITATION AS TRIBROMOPHENOL, $\text{HBr}$

**Procedure.**—To a large aliquot of the distillate from the tissue or stomach contents add saturated bromine water until a definite red color shows that excess bromine is present. Allow to stand for a few hours to form a well-crystallized precipitate. Filter through a weighed Gooch, or fritted glass, crucible. Wash with a little dilute bromine water and draw air through the crucible to remove free

<sup>28</sup> Harger, R. N., and Bridwell, E. G., *J. Biol. Chem.*, 123, 1, 1938.

In the calculation of results from the two procedures above, do not forget to employ the reciprocals of all aliquots used in the procedure.

### THALLIUM

Like lead, thallium is quantitatively removed from an alkaline cyanide solution and, if present, its red dithizone complex would accompany the lead dithizone complex in the method for lead described earlier. To separate the two, proceed as follows:

*Procedure.*—After reading its O.D., place the dithizone extract from the lead analysis in a small evaporating dish and heat to dryness on the steam bath. To the residue in the dish add 1 ml. of water, 1 ml. of concentrated HCl and a small crystal of  $\text{KClO}_3$ . Warm on the steam bath for 3 minutes, dilute with 10 ml. of water, and shake in a separatory funnel with two 10-ml. portions of ether. Pass the ether extracts through a dry filter paper and evaporate to dryness. Dissolve the residue in 10 ml. of the dilute  $\text{HNO}_3$  solution used for lead and extract with dithizone Solution II as per the last paragraph of the lead procedure, using one-fifth quantities of all reagents. If the dithizone extract retains its green color, thallium is absent.

If a red color should develop, extract further with dithizone Solution II and compare the O.D. of the combined extracts with that of thallium standards similarly treated.

To further confirm thallium, re-convert the dithizone complex to the trichloride, extract with ether as before, and evaporate the ether extracts to dryness. Dissolve the residue in 2 ml. of dil. HCl. Add a small crystal of sodium bisulfite and evaporate to about 0.5 ml. If thallium is present, the final solution will give the characteristic green flame test, will yield a yellow turbidity with KI solution and, on saturation with NaCl, will show a blue fluorescence under ultraviolet light.<sup>30</sup>

<sup>30</sup> Sill, C. W., and Peterson, H. C., *Anal. Chem.*, **21**, 1266, 1949.

In contrast to the natural product over which control is limited, the synthetic elastomers are prepared in ways affording control of the length of the polymer chain, the configuration of the monomer units in the chain, and control of the non-rubber constituents present in the raw product. Most of the elastomers synthesized today are prepared in emulsion or latex form resembling the natural product.

Coagulation of the latex, usually with salt and acid, yields a crumb or particulate slurry. This slurry is dried and baled by compression of the crumb into blocks of elastomer. Usually an antioxidant is added to the latex prior to coagulation to prevent spontaneous oxidation of the elastomer on the drier and in storage.

As a result of the method of preparation the raw polymer will then contain residues of the emulsifying agent both in alkaline and acid form, small amounts of various salts, and an organic antioxidant. Impurities in the various ingredients used, as well as possible contamination from the metallic equipment used, introduce small quantities of other materials in the raw elastomer. Iron is probably the largest and most important such contaminant. Traces of the polymerizing agent or agents may also be present and in some cases this also may be a source of iron in the raw polymer.

**Rubber Products.**—Nearly all products made from rubber or the synthetic elastomers are vulcanized or cross-linked by means of sulfur or a sulfur-containing agent. The mechanism of the vulcanization reaction is not completely understood nor is the structure of the final product actually known, but the result of the reaction is to provide a product superior to the raw material itself.

The vulcanization reaction is almost always carried out with more than sulfur and rubber as the ingredients. Organic accelerators of complex structure such as mercaptobenzothiazole, tetramethylthiuram disulfide, etc., serve to speed up the reaction and certain of these may be used to replace sulfur entirely as the vulcanizing agent.

Zinc oxide and stearic acid are both necessary either as such or as zinc stearate in order to obtain a satisfactory sulfur vulcanizate.

Other materials are usually added for a variety of reasons. First, there are reinforcing agents whose purpose is to improve wear properties, hardness, stiffness or some such physical property. Carbon blacks of various types are used as well as certain silica materials. Second, there are bulking agents whose function is to reduce the cost of the product. These may include such things as clays, barium carbonate or sulfate, magnesium carbonate, talc, etc. Third, pigments or colors are added to impart color to the finished product. Titanium oxide is probably the most important pigment for white products though zinc oxide, zinc sulfide, or lithopone are often used. Iron oxide is widely used for brown to reddish-colored articles while organic dyes provide a wide range of relatively brilliant colors. Naturally, carbon black is not used in conjunction with the coloring materials except with small amounts of zinc oxide which serves as an aid to the vulcanization reaction.

Oils, waxes, resins, etc., are used as plasticizing agents to impart certain processing characteristics to the compounded material or some particular property to the finished article.

These examples of some of the materials present in rubber products may give the reader some feeling for the complex system a rubber article presents to the analyst.

## RUBBER POLYMER NOMENCLATURE

The definitions of the types of polymers discussed in this chapter and of other types for which no standard methods of analysis exist are those established by the ASTM.<sup>1</sup> A system of abbreviations to simplify the use of this nomenclature is also included. While the major portion of this chapter is devoted to analysis of the R family of polymers, many members of the other families of polymers have rubberlike properties and occasional reference to some of them is made in this chapter. The following is an excerpt from this ASTM Recommended Practice.

**Elastomers and Rubbers**—1 Elastomers and Rubbers both in the dry and latex form shall be classified and coded from the chemical composition of the polymer chain in the following manner:

- M—Elastomers having a saturated chain of the polymethylene type
- N—Elastomers having nitrogen in the polymer chain
- O—Elastomers having oxygen in the polymer chain
- P—Elastomers having phosphorus in the polymer chain
- R—Rubbers or elastomers having an unsaturated carbon chain, for example, natural rubber and synthetic rubbers at least partly derived from diolefins
- Si—Elastomers having silicone in the polymer chain
- T—Elastomers having sulfur in the polymer chain
- U—Elastomers having carbon, oxygen and nitrogen in the polymer chain

**Family Designations**—2 The R family both in dry and latex form shall be defined by inserting the name of the monomer or monomers before the word rubber from which it was prepared (except for natural rubber). The letter immediately preceding the letter R shall signify the diolefin from which the rubber was prepared (except for natural rubber). Any letter or letters preceding the diolefin letter signifies the comonomer or comonomers. The following classification shall be used for members of the R family:

- BR—Butadiene rubbers
- IR—Isoprene rubbers, synthetic
- CR—Chloroprene rubbers
- NR—Isoprene rubber, natural
- ABR—Acrylate butadiene rubbers
- IIR—Isobutylene-isoprene rubbers
- NBR—Nitrile-butadiene rubbers
- NCR—Nitrile-chloroprene rubbers
- PBR—Pyridine-butadiene rubbers
- SBR—Styrene-butadiene rubbers
- SCR—Styrene-chloroprene rubbers
- SIR—Styrene-isoprene rubbers

<sup>1</sup> Tentative Recommended Practice for Nomenclature for Synthetic Elastomers and Latexes ASTM Designation D1418-61T

<sup>2</sup> When designating latex or latexes the terminology shall be for example SBR latex<sup>2</sup> or SBR latexes

## THE ANALYTICAL PROBLEM

*Reasons for Analysis.*—The success of large industry in the world today depends on rapid, accurate testing of products and raw materials as much as on mechanization of production and effective marketing.

Analysis of raw materials is necessary to the manufacturer in order to establish quality and price for his purchase; analysis at various stages of production is necessary for good process control; analysis serves as a means for checking behavior of product or for determining the cause of faulty products; analysis is used to detect factory errors; and finally, analysis serves as a control for consumers' specification of a finished product.

## COMPLETE ANALYSIS SCHEME

The greatest problem faced by an analyst who is not familiar with rubber is that of deciding what analyses are possible and which ones are necessary in order to obtain the desired information. As an aid to the solution of this problem there is included here a schematic diagram of the analyses that can be run on a vulcanized rubber compound. This diagram together with the definitions and descriptive material found in this chapter should enable the analyst to plan his analytical approach efficiently.

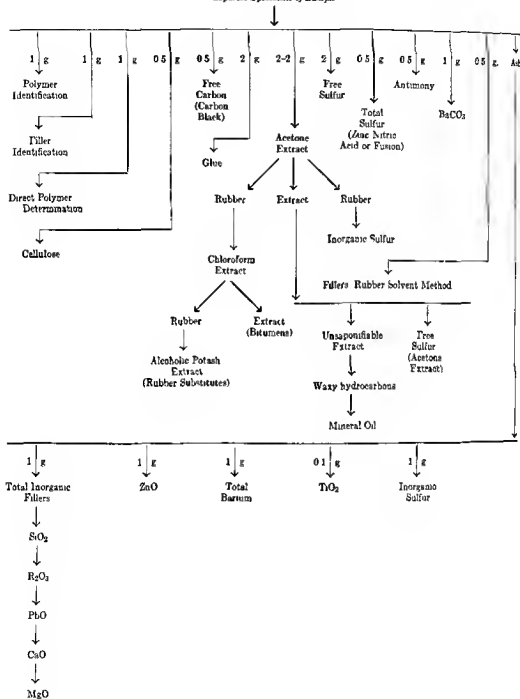
The sample weights given in the diagram are the nominal sample sizes for a single determination. It is frequently possible to use a somewhat smaller sample. The weights given under the heading of ash refer to original rubber sample. Since it is seldom necessary to run all of the listed analyses the sample requirement is not large.

The analysis scheme has been written to cover vulcanized rubbers. It can be applied to unvulcanized compounds in general if the chloroform extract is omitted.



## ANALYSIS SCHEME

## COMPLETE ANALYSIS OF A VULCANIZED RUBBER COMPOUND

*Separate Specimens of Sample*

# CRUDE RUBBER ANALYSIS

## NATURAL RUBBER

### INTRODUCTION

The analysis of crude natural rubber serves as a check on the evaluation or grade of natural rubber purchased. The important criteria are usually those affecting the stability and vulcanization characteristics of the rubber. Foreign matter or adulterants not affecting the above properties are of economic interest in establishing the price of the raw material. Among the analytical procedures in wide use are those for: Ash, Copper, Manganese, Iron, Acetone extract, Dirt, Volatile matter, Rubber Hydrocarbon, and Protein.

ASTM has issued tentative methods for these analyses under Designation D1278-61T.<sup>3</sup> The following methods described are primarily those of the ASTM except where noted. Attempts are made to give the latest procedures proved to be suitable for a standard method. In all cases, specimens are to be taken from a large sample homogenized as described in the section on Volatile Matter, page 2158.

### ASH

The determination of ash content of rubber products is only valid when the inorganic materials present are not decomposed by the ashing procedure. The same procedure for the determination of ash may be applied to both vulcanized and unvulcanized rubber. The muffle furnace procedure outlined is the preferred one. However, careful distillation of the sample over a very small flame without allowing the sample to ignite will be found suitable for ashing for tests on the ash. This flame procedure is not adequate for quantitative ash determinations.

**Apparatus.** Crucible.—An unetched porcelain crucible having a capacity of 50 ml. If copper is subsequently to be determined, a smooth unetched silica crucible is preferred, but a Vycor crucible or an ignited, acid-washed unetched No. 2 Coors porcelain crucible may be used.

**NOTE.**—In cases of dispute where the greatest accuracy is required, use a new, smooth silica crucible each time the test is run.

Muffle Furnace, with temperature indicator and control.

Filter Paper, Ashless, about 15 cm. in diameter.

**Procedure.**—Weigh a 5- to 6-g. specimen of homogenized rubber to the nearest 1 mg. and place it in a crucible previously ignited and weighed to the nearest 0.1 mg. Place the crucible and its contents in a furnace controlled at a temperature of  $550 \pm 25^\circ\text{C}$ . until free from carbon (**NOTE**). When ashing is complete, cool the crucible in a desiccator and then weigh it to the nearest 0.1 mg.

**NOTE.**—The rubber may be charred over a small flame or on a hot plate before it is placed in the furnace. When the rubber is not previously charred before placing it in the furnace, the crucibles shall be placed on a suitable tray to permit placing them in the

<sup>3</sup> Tentative Methods for Chemical Analysis of Natural Rubber, ASTM Designation D1278-61T.

furnace simultaneously and the door of the furnace shall then be kept closed for at least 1 hour while flammable vapors are evolved. If copper, manganese or iron is to be determined the specimen shall be wrapped in a 15 cm ashless filter paper previous to ashing.

**Calculation**—Calculate the ash content as follows:

$$A = \frac{C - B}{D} \times 100$$

where  $A$  = the percentage of ash,

$D$  = weight of the specimen

$B$  = weight of the empty crucible and

$C$  = weight of the crucible plus ash

## COPPER

The amounts of copper that are involved in the stability of raw natural rubber are so small, order of 0.50 p.p.m., that an extremely sensitive test is required for the analysis. The photometric method outlined meets this requirement. However, every precaution must be taken to prevent contamination of the glassware, furnace, and solvents used in the procedure. It is recommended that the glassware used in this determination be reserved for this use only and not used as general laboratory equipment.

**Apparatus** Photoelectric Photometer—A spectrophotometer or filter photometer suitable for measurements at approximately 435 m $\mu$ . Absorption cells 1 to 5 cm. in path length may be used. Cells 2 to 5 cm. in path length are preferred.

**Reagents and Materials** Ammonium Hydroxide (sp. gr. 0.90)—Concentrated ammonium hydroxide ( $\text{NH}_4\text{OH}$ )

Carbon Tetrachloride ( $\text{CCl}_4$ )

Citric Acid Solution (500 g. per liter)—Dissolve 50 g. of citric acid in 100 ml. of  $\text{H}_2\text{O}$ .

Copper Sulfate Standard Solution (1 ml. = 0.1 mg. Cu)—Dissolve 0.393 g. of copper sulfate ( $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ ) in water, add 3 ml. of concentrated sulfuric acid ( $\text{H}_2\text{SO}_4$ , sp. gr. 1.84) and dilute to 1 l. with water. This solution should remain stable for at least a month.

Copper Sulfate Standard Solution (1 ml. = 0.01 mg. Cu)—Dilute 10 ml. of the  $\text{CuSO}_4$  solution (1 ml. = 0.1 mg. Cu) to 100 ml. with water. Make up this solution fresh each day.

Nitric Acid (1:2)—Mix 1 volume of concentrated nitric acid ( $\text{HNO}_3$ , sp. gr. 1.42) with 2 volumes of water.

Sodium Diethyldithiocarbamate Solution (1 g. per liter)—Dissolve 0.1 g. of sodium diethyldithiocarbamate in water and dilute to 100 ml. Store in an amber bottle away from strong light. Renew the solution every 2 weeks.

Sodium Sulfate, Anhydrous ( $\text{Na}_2\text{SO}_4$ )

**Preparation of Calibration Curve**—(a) Make up a series of standard solutions each containing 15 ml. of  $\text{HNO}_3$  (1:2) and 5 ml. of citric acid diluted with water to not more than 50 ml. To these solutions add portions of copper solution (1 ml. = 0.01 mg. Cu) ranging from 0 to 10 ml. followed by excess  $\text{NH}_4\text{OH}$  and 20 ml. of sodium diethyldithiocarbamate solution. Let the solutions stand for 20 minutes in subdued light. Extract the copper complex from each solution with three or four 5 ml. portions of carbon tetrachloride. Collect these portions dry them with  $\text{Na}_2\text{SO}_4$  and make up to 25 ml. in volumetric flasks.

(b) Measure the absorbance of each solution in the series at approximately 435  $m\mu$ , using as the reference solution the solution to which no copper was added. Use cells of the same path length as used in Procedure (d).

(c) Prepare a calibration curve by plotting the relationship between copper concentration and absorbance. The calibration curve should be checked whenever necessary, depending on local conditions and on the type of instrument used.

**Procedure.**—(a) Ash the specimen as described in the procedure for Ash Determination, page 2151. Ash a blank consisting of the filter paper in the same manner and carry it through the procedure in the same manner as the sample. Add 15 ml. of  $\text{HNO}_3$  (1:2) to the crucible, and digest the mixture on a steam bath for 30 to 60 minutes. Wash the contents of the crucible into a small beaker or flask, dilute with water to not more than 25 ml., and filter into a second beaker.

(b) Add 5 ml. of citric acid to the filtrate, followed by  $\text{NH}_4\text{OH}$  until the solution is strongly alkaline. Cool the solution, transfer to a separatory funnel, and add 20 ml. of sodium diethyldithiocarbamate solution. After standing for about 20 minutes in subdued light, extract the solution by shaking vigorously with three or four 5-ml. portions of carbon tetrachloride. If the last extract is not colorless, continue the extraction until it is.

(c) After separation, draw off the carbon tetrachloride extracts and collect them in a stoppered flask containing about 0.1 g. of anhydrous  $\text{Na}_2\text{SO}_4$ . If turbidity persists after standing for 30 minutes, make further small additions of  $\text{Na}_2\text{SO}_4$  until the solution becomes clear. Then decant the solution through a plug of glass wool or through a small filter paper into a 25-ml. volumetric flask. Make up to volume with carbon tetrachloride, and transfer to the cell of a photoelectric photometer.

(d) Measure the absorbance at approximately 435  $m\mu$ , using the blank solution as the reference solution.

**NOTE.**—If the absorbance is less than 0.30, use absorption cells of longer path length if maximum accuracy is desired. Obtain the calibration curve using the same path length and shape cells as used in the procedure. If the absorbance is greater than 0.8, use cells of shorter path length or dilute the sample solution with  $\text{CCl}_4$ , if maximum accuracy is desired. Disregard this note if copper is to be reported only to the nearest 0.5 p.p.m.

(e) Determine the concentration of copper in the test solution from the absorbance reading and the calibration curve. Express the result as parts of copper per million parts of the rubber specimen.

## MANGANESE

Similar precautions to those given for the copper determination are in order for this procedure as again a very sensitive test is required. The order of magnitude of the manganese content is 0–40 p.p.m.

**Apparatus.** Photoelectric Photometer.—A spectrophotometer or filter photometer suitable for measurements at approximately 525  $m\mu$  with absorption cells 1 to 5 cm. in path length. The 5-cm. cells are preferred.

**Reagents.** Manganese Sulfate, Standard Solution (1 ml. = 1 mg. Mn).—Dissolve 0.77 g. of manganese sulfate ( $\text{MnSO}_4 \cdot \text{H}_2\text{O}$ ) in water, add 2 ml. of sulfuric acid ( $\text{H}_2\text{SO}_4$ , sp. gr. 1.84), and dilute to 250 ml. with water. This solution should be stable for at least a month.

Manganese Sulfate, Standard Solution (1 ml. = 0.02 mg. Mn).—Dilute 10 ml. of the  $\text{MnSO}_4$  solution (1 ml. = 1 mg. Mn) to 500 ml. with water. Make up this solution fresh each day.

**Orthophosphoric Acid (85 to 90 per cent)**—Concentrated orthophosphoric acid ( $\text{H}_3\text{PO}_4$ )

**Potassium Hydrogen Sulfate ( $\text{KHSO}_4$ )**

**Potassium Periodate ( $\text{KIO}_4$ )**

**Potassium Permanganate Rinse Solution (0.03 g per l)**—Dissolve 0.03 g of potassium permanganate ( $\text{KMnO}_4$ ) in water and dilute to 1 l

**Sulfuric Acid (1.19)**—Mix 1 volume of concentrated sulfuric acid ( $\text{H}_2\text{SO}_4$  sp gr 1.84) with 19 volumes of water

**Preparation of Calibration Curve**—(a) Prepare a series of standard solutions by diluting portions of  $\text{MnSO}_4$  solution (1 ml 0.02 mg Mn) ranging from 0 to 20 ml to about 25 ml with water adding 20 ml  $\text{H}_2\text{SO}_4$  (1.19) and 0.3 g  $\text{KIO}_4$ . Heat each solution as described in Procedure (c)

**NOTE**—If the expected manganese content is below 20 ppm the calibration curve need not extend beyond 10 ml of standard  $\text{MnSO}_4$  solution

(b) Cool the solutions transfer to 50 ml volumetric flasks and dilute to volume. Measure the absorbance at approximately 525  $\text{m}\mu$  using the solution to which no manganese was added as the reference solution. Use absorption cells having the same length and shape as used in Procedure (d)

(c) Prepare a calibration curve by plotting the relationship between manganese concentration and absorbance. The calibration curve should be checked whenever necessary depending on local conditions and on the type of instrument used

**Procedure**—(a) Wrap a 10 to 12 g specimen in a 15 cm ashless filter paper place 5 g of  $\text{KHSO}_4$  on top of the specimen in a porcelain crucible and ash in accordance with the procedure for Ash Determination page 2151. Ash a blank consisting of the filter paper and the  $\text{KHSO}_4$  in the same manner and carry it through the procedure in the same manner as the sample

(b) Add 20 ml of  $\text{H}_2\text{SO}_4$  (1.19) to the crucible and heat the crucible on a steam bath for 30 minutes crushing the residue occasionally with a glass rod to facilitate dissolution. Filter the solution into a 150 ml beaker rinse the crucible with water and pass the rinsings also through the filter

**NOTE**—A filter crucible is preferred although filter paper may be used if it in no way affects the final color development. In either case the filtrate shall be perfectly clear

(c) Add 3 ml of  $\text{H}_3\text{PO}_4$  and 0.3 g of  $\text{KIO}_4$  to the filtrate and evaporate by careful boiling to a volume of less than 50 ml over a period of approximately 75 minutes. Transfer the solution to a 50 ml volumetric flask and after cooling to room temperature dilute the solution with water to the 50 ml mark

**NOTE**—If a turbidity appears at this point or after transfer of the solution to an absorption cell it is probably due to crystallization of  $\text{KIO}_4$ . In this case the solution must be allowed to stand until it is clear or it must be refiltered and reheated in accordance with Procedure (b) and (c) but without further addition of  $\text{KIO}_4$

(d) Rinse the cell of the photoelectric photometer with the  $\text{KMnO}_4$  rinse solution then with water and finally with the test solution. Fill the cell with the test solution and measure its absorbance at approximately 525  $\text{m}\mu$  using the blank solution as a reference solution

**NOTE**—If 1 cm path length cells are used report the results only to the nearest 1 ppm. If greater accuracy is desired use a cell of greater path length preferably a 5 cm cell in order to obtain absorbance readings between 0.3 and 0.8

(e) Determine the concentration of manganese in the test solution from the absorbance reading and the calibration curve. Express the result as parts of manganese per million parts of the rubber specimen.

### IRON

The photoelectric photometer method given is superior in reproducibility to any visual method for analysis in the range of 0–40 p.p.m. While the iron content may frequently exceed 40 p.p.m., this figure may be considered an upper limit in that acceptable rubbers are nearly always below 40 p.p.m.

**Apparatus.** *Photoelectric Photometer.*—A spectrophotometer or filter photometer suitable for measurements at approximately 510 m $\mu$  with absorption cells 1 to 3 cm. in path length.

**Reagents.** *Buffer Solution.*—Dissolve 123 g. of anhydrous sodium acetate in water, add 90 ml. of acetic acid, and dilute the mixture with water to 500 ml.

**NOTE.**—If this buffer solution gives highly colored reference solutions, alternative buffer solutions can be prepared by dissolving 60 g. of sodium hydroxide (NaOH) or 80 g. of sodium carbonate (Na<sub>2</sub>CO<sub>3</sub>) in 200 ml. of water, adding 180 ml. of acetic acid, and diluting to 500 ml.

*Hydrochloric Acid* (sp. gr. 1.19).—Concentrated hydrochloric acid (HCl).

*Hydroxylamine Hydrochloride Solution* (100 g. per liter).—Dissolve 10 g. of hydroxylamine hydrochloride in 100 ml. of water.

*Iron, Standard Solution* (1 ml. = 0.1 mg. Fe).—Dissolve 0.7021 g. of ferrous ammonium sulfate (Fe(NH<sub>4</sub>)<sub>2</sub>(SO<sub>4</sub>)<sub>2</sub>·6H<sub>2</sub>O) in water containing 3 ml. of concentrated hydrochloric acid (HCl, sp. gr. 1.19) and dilute to 1000 ml. with water. This solution should remain stable for at least a month.

*Iron, Standard Solution* (1 ml. = 0.01 mg. Fe).—Dilute 10 ml. of the iron solution (1 ml. = 0.1 mg. Fe) to 100 ml. with water. The iron solution must be made up fresh each day.

*1,10-Phenanthroline Solution* (1 g. per l.).—Dissolve 0.5 g. of 1,10-phenanthroline monohydrate in hot water and dilute to 500 ml.

**Preparation of Calibration Curve.**—(a) Prepare a series of standard solutions by pipetting portions of 0, 5, 10, 15, and 20 ml. of iron solution (1 ml. = 0.01 mg. Fe) into 50-ml. volumetric flasks. To each add 1 ml. of HCl.

(b) Make an analysis of each of the standard solutions as described in *Procedure* (b) and (c), starting with the addition of the buffer solution and continuing through the measurement of the absorbance, using the solution containing no added iron as the reference solution.

(c) Prepare a calibration curve by plotting the relationship between iron concentration and absorbance. The calibration curve should be checked whenever necessary, depending on local conditions and on the type of instrument used.

**Procedure.**—(a) Ash a 10- to 12-g. specimen of homogenized rubber according to the ashing procedure described in the procedure for Ash Determination, page 2151, except that the temperature shall be maintained at 525  $\pm$  25°C. and the sample shall be wrapped in a 15-cm. ashless filter paper. Ash a blank consisting of the filter paper and carry it through the procedure in the same manner as the sample. Add 5 ml. of HCl and 5 ml. of water to the crucible and digest the mixture on a steam plate for 30 to 60 minutes. If the solution has a deep yellow color, indicating the presence of much iron, add 5 ml. more of HCl and continue the digestion for

30 minutes more. Filter the solution, collect the filtrate in a 50 ml volumetric flask, and dilute to the 50 ml mark.

(b) Transfer an aliquot containing not more than 2 ml of HCl to a 50 ml volumetric flask. Add 10 ml of the buffer solution, then 1 ml of hydroxylamine solution, and 10 ml of 1,10 phenanthroline solution. Dilute the solution to the mark with water and allow to stand for 10 minutes. Treat an equal aliquot of the blank solution by the same procedure.

(c) Fill the cell of the photoelectric photometer with this solution and measure the absorbance at a wavelength of approximately 510  $m\mu$ , using the treated blank aliquot as a reference solution. If the absorbance is greater than 0.8 repeat this step using a smaller aliquot. If the absorbance is below 0.3, repeat with a larger aliquot if this is possible.

(d) Determine the concentration of iron in the test solution from the absorbance reading and the calibration curve and express the value as parts of iron per million parts of the rubber specimen.

### ACETONE EXTRACT

The apparatus shown is used for all Soxhlet type extractions of both vulcanized and unvulcanized rubber. Acetone extraction should not be used on raw SBR types of rubber due to the presence of soap in these rubbers. The soap may cause polymerization of the acetone to give high results for acetone extract. The azeotrope of ethanol and toluene is used for raw SBR rubbers in a non-Soxhlet extraction procedure described under Synthetic Rubber, Organic Acid, page 2181.

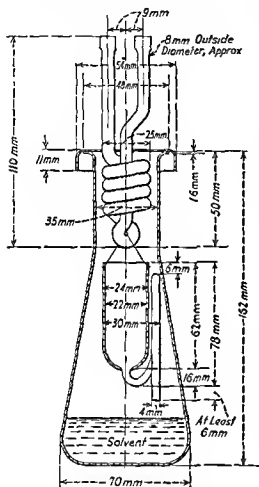


Fig. 43-1 Extraction Apparatus

**Apparatus.** Extraction Apparatus.—The extraction apparatus used for acetone extract, chloroform extract, or for total extract, is of the general type and dimensions shown in Fig. 43-1.

**Procedure.**—Place a weighed specimen of approximately 2 g in a filter paper. If the specimen is in the form of a sheet, cut it with scissors into strips 3 to 5 mm. in width. If the specimen may become tacky during the extraction, take care that adjacent portions are separated by paper. Fold the paper so that it will fit in the extraction cup and suspend the cup in a weighed extraction flask containing 50 to 75 ml of acetone. (Prior to the weighing of the extraction flask, it shall have been dried for 2 hours at  $70 \pm 5^\circ\text{C}$  and cooled in a desiccator to the temperature

of the balance.) Extract the specimen continuously for 16 hours, heating at a rate such that the time required to fill and empty the siphon cup will be between 2.5 and 3.5 minutes. (Hard rubber, and any soft rubber specimen having a ratio of total sulfur to rubber hydrocarbon in excess of 10%, shall be extracted for 72 hours.) Carefully note all characteristics of the extract, both when hot and cold. Evaporate off the acetone over a steam bath, using a gentle current of filtered air to prevent boiling. Remove the flask from the steam bath just prior to the disappearance of the last traces of solvent to prevent loss of extract. Continue the passage of air through the flask for 10 minutes to remove the remaining solvent and dry the flask for 2 hours at  $70 \pm 5^\circ\text{C}$ . in an air bath. Cool in a desiccator to the temperature of the balance and weigh.

Calculation.—Calculate the percentage of acetone extract as follows:

$$\text{Acetone extract, per cent} = \frac{A}{B} \times 100$$

where  $A$  = grams of extract, and

$B$  = grams of specimen used.

### DIRT CONTENT

This procedure is intended to give the purchaser some idea of the cleanliness of the raw natural rubber he is purchasing. Obviously, sampling is extremely important in this test and due consideration to sampling must be given.

**Apparatus.** Sieve.—A No. 325 (44-micron) sieve.

**Reagents.** Petroleum, Light, boiling between  $60^\circ$  and  $80^\circ\text{C}$ .

**Rubber Peptizing Agent.**—A suitable rubber peptizing agent is a commercial mixture of xylene thiols, such as that designated RPA #3, available from E. I. DuPont de Nemours and Co.

**Rubber Solvent,** boiling above  $130^\circ\text{C}$ .

**Procedure.**—Weigh a 10- to 12-g. specimen of homogenized rubber to the nearest 0.1 g. and cut into bits having a maximum dimension of less than 3 mm. Place the bits in a 250-ml. conical flask and cover with 150 ml. of rubber solvent containing about 0.5 g. of peptizing agent. Heat the mixture and maintain it at a temperature of  $125$  to  $130^\circ\text{C}$ . (NOTE) until dissolution is complete (about 3 hours).

Pour the hot solution through a sieve previously weighed to the nearest 0.1 mg. Wash the flask three times with about 25 ml. of hot rubber solvent by pouring the solvent through the sieve. Transfer any dirt remaining in the flask to the sieve by means of a jet of light petroleum and wash until free of rubber solution. Dry the sieve containing the dirt at  $100 \pm 5^\circ\text{C}$ . and weigh to the nearest 0.1 mg.

Calculation.—Calculate the dirt content as follows:

$$D = \frac{C - B}{A} \times 100$$

where  $D$  = percentage of dirt,

$A$  = weight of the specimen,

$B$  = weight of the clean, dry sieve, and

$C$  = weight of the sieve plus dirt.

NOTE.—Overheating or boiling may cause gelling or charring.



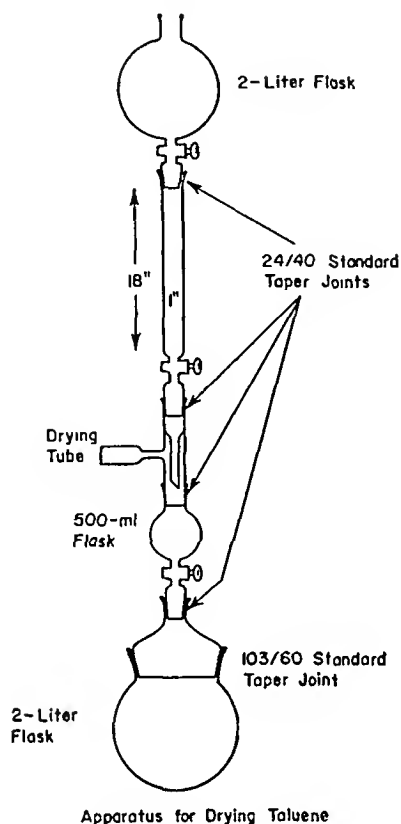


FIG. 43-2. Apparatus for Drying Toluene.

the trap to cool for 15 minutes in water bath at room temperature. Lower the leveling bulb until the water collected in the trap is drawn into the graduated portion of the capillary.

NOTE.—It is convenient to bring one end of the water column to a fixed reference point on the capillary. Read the length of the column of water in the capillary to the nearest millimeter.

Calculation.—

$$\text{Moisture, per cent} = \frac{100(BC)}{A}$$

where  $A$  = the weight of the original sample, in grams.

$B$  = the length of the water column in millimeters.

$C$  = the calibration factor determined for the apparatus in the following matter.

**Preparation and Calibration of Equipment.**—Coat the clean and air-dried (not oven) apparatus with a thin film of silicone resin by pouring a solution of 5% methyl chlorosilane in toluene into the trap, capillary, and condenser. Allow it to remain in the apparatus about 5 minutes. Pour the solution out and dry the

## ISOPRENE POLYMER (NR or IR)

The direct method is based on an oxidation of the isoprene polymer with chromic acid to yield acetic acid. The acetic acid yield has been found to be 75% of the theoretical isoprene content by tests on purified natural rubber. This 75% figure is highly reproducible though unaccountably low. The acetic acid formed is distilled and titrated after aeration to remove  $\text{CO}_2$ . The procedure is suitable for crude and vulcanized rubber products and for certain mixtures. The procedure

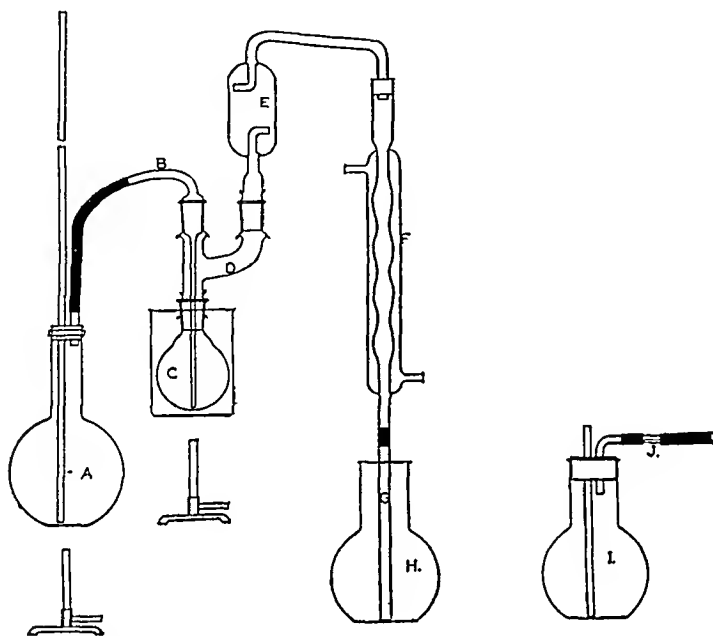


FIG. 43-4. Apparatus for Direct Determination of Isoprene Polymer: A, Steam Generating Flask, 1000-ml.; B, Steam Tube, Standard Taper 24/40 Joint; C, Digestion Flask, 300-ml.; D, Connecting-Tube, Standard Taper 24/40 Joints; E, Connecting Bulb, Standard Taper 24/40 Joints; F, Condenser; G, Adapter; H, Receiving Flask, 1000-ml.; I, Aeration Assembly; J, Capillary Tube.

given is a combination of excerpts from ASTM Designations D297-61T<sup>16</sup> and D1278-61T<sup>3</sup> in order to make it applicable to crude and to vulcanized rubber samples.

**Apparatus.** Digestion and Distillation Assembly.—The digestion and distillation apparatus shown in Fig. 43-4 may be conveniently assembled on a ring-stand with a tripod foot. The use of rubber or cork connections should be avoided where they might come into contact with the digestion mixture.

Aeration Assembly, consisting of the parts labeled I and J in Fig. 43-4.—The assembly should fit the receiving flask of the distillation assembly. The stopper should carry two glass tubes, one of which extends to the bottom of the flask and the other enables a vacuum line to be attached to withdraw air from the top of the flask. The capillary tube, J, when connected to the vacuum line should maintain through the receiving flask an air flow of approximately 2 l. per minute.

If the vacuum is less than 30 mm of mercury, a capillary tube approximately 10 cm in length with an 0.75 mm bore will maintain the required air flow. Since it is essential that the aeration be maintained at a rate within 10 to 20 per cent of 2 l per minute, each capillary shall be tested before use. The following method may be used. Invert a graduate over a beaker filled with water and evacuate the air through the capillary by means of a tube extending up into the graduate. The rate of air flow will be the same as the rate at which the water fills the graduate.

**Reagents** **Chromic Acid Digestion Mixture**—Dissolve 200 g of chromium trioxide ( $\text{CrO}_3$ ) in 500 ml of water and add 150 ml of concentrated sulfuric acid ( $\text{H}_2\text{SO}_4$  sp gr 1.84).

**Phenolphthalein Indicator, Alcoholic Solution** (2 g per l)—Dissolve 0.2 g of phenolphthalein in 100 ml of ethanol.

**Sodium Hydroxide, Standard Solution** (0.1 N)—Prepare and standardize a 0.1 N solution of sodium hydroxide ( $\text{NaOH}$ ).

**Preparation of Specimen** (a) **Vulcanized Rubber Products**.—Weigh a sufficient amount of the sample sheeted to a thickness of 0.5 mm to contain approximately 0.3 g of isoprene polymer. Wrap the specimen loosely in filter paper and extract by the total extract procedure as described on p. 220. After extraction dry the specimen in an oven at  $100^\circ\text{C}$  for 1 hour.

(b) **Unvulcanized Rubber**.—Prepare a sample of the rubber by sheeting it to a thickness of not greater than 0.5 mm (0.02 in.) in such a manner that specimens when taken from the sheet will retain this thickness and will not be sticky. Weigh a specimen of not over 0.3 g to the nearest 0.1 mg and cut it into four or five pieces of about equal size.

Extract the sample with acetone in accordance with Method for Acetone Extract, p. 220, protecting it from the light during the extraction. Dry the extracted rubber in an oven for 1 hour at 70 to  $75^\circ\text{C}$ .

**NOTE**—Milling on an even speed mill can be used for this preparation. The use of an odd speed mill at low friction ratios may be satisfactory if the above requirements can be met. Appreciable breakdown of the rubber must be avoided.

**Procedure**—Place sufficient water in the receiving flask *H* to cover the end of adapter *G*. Mark the outside of the digestion flask *C* at a point indicating the level at which the flask contains 75 ml of liquid and transfer  $50 \pm 1$  ml of the chromic acid oxidation mixture to the digestion flask.

Lift the steam inlet tube to insert the weighed and extracted specimen. After replacing the steam inlet tube raise a boiling water bath to immerse the digestion flask and heat the flask at  $100^\circ\text{C}$  for 1 hour. At the conclusion of this period remove the water bath and continue heating directly by a Bunsen burner.

**NOTE**—It is not necessary to remove quantitatively any filter paper adhering to the specimen before transferring it to the digestion flask, since the interference of small amounts of cellulose is negligible.

Some specimens tend to float in the reagent solution and do not react completely. It is sometimes possible to obtain more complete reaction by adding the specimen to the reaction flask before adding the chromic acid oxidation mixture.

Pass steam from a suitable generator *A* into the flask. When the volume of liquid in the flask has increased to 75 ml adjust the heat beneath the flask to maintain this volume and continue the distillation until about 500 ml have collected in the receiving flask *H*. This operation will take about 45 minutes.

At the finish of the distillation raise the condenser *F* and adapter *G* with water

and add the rinsings to the distillate. Reduce the temperature of the distillate to below 25°C., and remove dissolved carbon dioxide by aeration. This may be carried out by inserting into the receiving flask *H*, the aeration assembly *I* and *J*, and drawing air through the liquid at a rate of  $2 \pm 0.3$  l. per minute for 30 minutes.

After completion of the aeration, remove the tube from the flask and rinse with water, collecting the washings in the flask. Add phenolphthalein indicator, and titrate the solution with 0.1 *N* NaOH solution.

Make a blank determination, using the same quantities of reagents and the same conditions of test as for the sample. The sodium hydroxide titration blank should not exceed 0.3 ml.

Calculation.—Calculate the isoprene polymer content as follows:

$$R = \frac{(V_s - V_b)N}{W} \times 9.08$$

where *R* = percentage of isoprene polymer,

*V<sub>s</sub>* = ml. of 0.1 *N* NaOH solution required for titration of the sample,

*V<sub>b</sub>* = ml. of 0.1 *N* NaOH solution required for titration of the blank,

*W* = weight of the specimen, in g., and

*N* = normality of NaOH used. This calculation is based on a 75% yield of acetic acid from the isoprene polymer. Limitations as to type of materials analyzed by this procedure and interference from the usual compounding ingredients are summarized in Tables 43-1 and 43-2.

TABLE 43-1. DEGREE OF INTERFERENCE OF RUBBER COMPOUNDING INGREDIENTS

Compounding Ingredient	Interference
Combined sulfur . . . . .	none in normal soft cures
Carbon black . . . . .	none as tested in tread stocks
Cellulose . . . . .	negligible, 2 per cent or less of its weight reacts as if it were isoprene polymer
Asphaltic hydrocarbon (mineral rubber)	removed by acetone and chloroform extraction. If not extracted, approximately 45 per cent of its weight reacts as if it were isoprene polymer
Factice, brown . . . . .	negligible, after acetone and chloroform extraction
Vistanex . . . . .	virtually unattacked

## PROTEIN

The protein content of raw natural rubber may be determined on the acetone extracted material by a modification of the ASTM D982-52 procedure given in the section on Nitrogen Content of NBR Rubbers, page 2172, using a factor of 6.25 to

TABLE 43-2 BEHAVIOR OF RUBBER-LIKE MATERIALS IN CHROMIC ACID OXIDATION PROCEDURE

Material	Value Obtained
Hard rubber (NR or IR products)	approximately 50 per cent of its weight reacts as if it were isoprene polymer
Balata (NR) TR	approximately equivalent to rubber approximately 18 per cent of its weight reacts as if it were isoprene polymer
NBR	approximately 1.5 to 2 per cent of its weight reacts as if it were isoprene polymer
SBR	approximately 3 per cent of its weight reacts as if it were isoprene polymer
CR	approximately 3 per cent of its weight reacts as if it were isoprene polymer if a modification of the procedure is used to avoid the interference of chlorine <sup>a</sup>

<sup>a</sup> This modification consists of adding neutral KI solution to the distillate after aeration and titrating any iodine that may be released with neutral  $\text{Na}_2\text{S}_2\text{O}_3$  solution before proceeding with the titration with 0.1 *N* NaOH solution

convert the per cent nitrogen to per cent protein. Because grading of natural rubber is often done on the basis of nitrogen content, the procedure is also useful on the unextracted crude rubber. The nitrogen content is a measure of quality to the extent that it detects the presence of extra protein or other nitrogenous matter resulting from the inclusion of tree scrap, bark or skim latex rubber in the bale of rubber.

The procedure given in the section on Nitrogen Content of NBR Rubbers page 2172, must be modified as follows because of the low nitrogen content and the large sample necessary for analysis. High grades of rubber will not contain more than about 0.5% nitrogen. Poor grades may run as high as 2%. Use a 2 g specimen of the homogenized rubber sample. Add 60 ml of sulfuric acid for digestion and about the same quantity of catalyst and sodium sulfate as specified. Approximately 100 ml of the sodium hydroxide solution will be necessary to provide the desired excess of base prior to distillation.

## SYNTHETIC RUBBERS

**Introduction.**—There have been few attempts to provide standard methods for analysis of crude synthetic rubbers, particularly for the less common "specialty"

rubbers. Some methods do exist for the more common rubbers. These, together with some newer methods that are well on their way to becoming standard methods by virtue of long usage, are discussed in this section.

The basic needs in this field are identification of types of rubbers, determination of composition of copolymers and determination of certain common impurities and additives found in the crude rubbers as supplied by the manufacturers.

## IDENTIFICATION OF SYNTHETIC RUBBERS— CHEMICAL METHODS

**Introduction.**—The ASTM <sup>5,16</sup> has published methods that are rapid and simple for the identification of the common individual rubber polymers and copolymers used as synthetic rubbers. The methods are based on the papers by Burchfield <sup>6</sup> and on information found in "The Services Rubber Investigations User's Memorandum, No. U9.<sup>7</sup> They are also applicable to analysis of rubber compounds and, in a few cases, to mixtures of polymers. Definitions and nomenclature referred to in this section appear in the introduction, page 2148. Unless otherwise specified the methods are applicable only to the "R" family of rubbers. The following is an abstract from the latest of the above mentioned ASTM methods.<sup>16</sup>

**Scope.**—This scheme is for use in the identification of IR, CR, NR, IIR, NBR, and SBR type rubber polymers when each is present alone as a rubber or in a rubber product. Use of the scheme on mixtures of rubber polymers is not recommended unless the validity of the tests has been confirmed on known mixtures.

### IDENTIFICATION BY PYROLYSIS PRODUCTS

**Apparatus.** Distillation Apparatus.—Test tubes, 10 by 75 mm., equipped with a glass condensing tube about 4 mm. in outside diameter attached to the test tube by means of a cork stopper. The condensing tube shall be bent at least 90 degrees, and shall extend about 100 mm. beyond the bend.

**Receiver.**—Test tubes, 10 by 75 mm., for collecting distillate.

**Test Tubes,** 16 by 150 mm.

**Reagents.** **Solution I.**—Dissolve 1.0 g. of *p*-dimethylaminobenzaldehyde and 0.01 g. of hydroquinone in 100 ml. of absolute methanol. Add 5 ml. of HCl and 10 ml. of ethylene glycol. Adjust the specific gravity to 0.851 at 25/4°C. by the addition of a calculated amount of methanol or ethylene glycol. The reagent is stable over a period of several months when stored in a brown bottle.

**Solution II.**—Dissolve 2.00 g. of sodium citrate ( $2\text{Na}_3\text{C}_6\text{H}_5\text{O}_7 \cdot 11\text{H}_2\text{O}$ ), 0.2 g. of citric acid, 0.03 g. of bromocresol green, and 0.03 g. of Metanil yellow in 500 ml. of water.

**Procedure.**—Strip the rubber from any adhering fabric. Place 0.5 g. of the sample in a test tube and attach the side arm. Heat with a microburner or very small Bunsen flame until the sample begins to decompose. When vapors appear at the mouth of the side arm, immerse the end beneath the surface of 1.5 ml. of Solution II contained in the receiver test tube. After it is evident whether a color change will take place or not, remove the tube and continue the distillation into 1.5 ml. of Solution I in another test tube. Permit the receivers to cool, and shake. Note whether the drops sink or float in Solution I and note the color changes in

<sup>5</sup> Tentative Methods of Identification and Quantitative Analysis of Synthetic Elastomers, ASTM Designation: D833-46T.

<sup>6</sup> Burchfield, H. P., Ind. Eng. Chem., Anal. Ed., 16, 424 (1944); Ibid., 17, 806 (1945).

<sup>7</sup> British Ministry of Supply, Admiralty, Ministry of Aircraft Production, London (1941).

both solutions Transfer Solution I to a 16 by 150 mm test tube and add 5 ml of absolute methanol Heat on a water bath at 100°C for 3 minutes and note the color that develops Record all observations and classify the material by means of Table 43 3

TABLE 43 3 PYROLYSIS TEST

Rubber Polymer	Solution I		Solution II
	Initial Color	Color after Heating	Color
Blank	pale yellow	pale yellow	green
CR	yellow	yellow	red
NBR	orange-red	red	green
SBR	yellow-green	green	green
NR or IR	brown	violet blue	green
IIR	yellow (drop let floats)	pale blue-green	green

## IDENTIFICATION BY SPOT TESTS

**Reagents CR NBR Spot Test Papers**—Dissolve 2 0 g of cupric acetate and 0 25 g of Metanil yellow in 500 ml of methanol Impregnate filter paper squares with the solution dry and cut into strips

**CR NBR Wetting Solution**—Dissolve 2 5 g of benzidine dihydrochloride in a mixture of 500 ml of methanol and 500 ml of water Add 10 ml of an aqueous solution of hydroquinone (0 1%) Store in a brown bottle

**NOTE**—A precipitate which usually forms on standing does not affect the efficiency of the solution If the solution is protected from light and air it can be used for several months

**IIR Spot Test Papers**—Use blank filter paper strips

**IIR Wetting Solution**—Add 5 0 g of yellow mercuric oxide ( $\text{HgO}$ ) to a mixture of 15 ml of  $\text{H}_2\text{SO}_4$  and 80 ml of water Bring to a boil and continue heating until the oxide dissolves Cool and dilute to 100 ml with water

**SBR NR IR Spot Test Papers**—Impregnate filter paper squares with a solution of 3 g of *p* dimethylaminobenzaldehyde and 0 05 g of hydroquinone in 100 ml of ethyl ether Dry and cut into strips

**NOTE**—Papers stored in brown glass bottles are stable for several weeks but will lose their efficiency if stored in light

**SBR NR IR Wetting Solution**—Dissolve 30 g of trichloroacetic acid in isopropanol and dilute to 100 ml with isopropanol (**Caution**—Avoid contact of this reagent with the skin)

**Procedure**—Wet a strip of each type of spot test paper with the corresponding wetting solution and hold each in turn in a parallel position about 5 mm above

the surface of a heating element that is pressed against the sample. Record the colors obtained and classify the sample by means of Table 43-4.

TABLE 43-4. SPOT TEST

Rubber Polymer	CR-NBR Test	IIR Test	SBR-NR-IR Test
CR.....	red	blank <sup>a</sup>	green
NBR.....	green	pale brown	yellow-green
SBR.....	blank <sup>a</sup>	brown	blue-green
NR or IR.....	blank <sup>a</sup>	brown	blue
IIR.....	blank <sup>a</sup>	yellow	pale lavender

<sup>a</sup> Blank color tests may be pale brown rather than colorless.

The heating element may be an electrically-heated knife or iron or an iron or file tip heated by a flame. It should be hot enough to cause dense fumes of pyrolysis product to be produced but not sufficiently hot to ignite the rubber. With vigorous evolution of fumes, a test may be carried out in 4 to 6 seconds. Care should be taken to obtain a good color response on the side facing the fumes without scorching the paper or the impregnating materials.

### CONFIRMATORY TESTS

*Reagents.* Acetone.

Bromine.

Carbon Tetrachloride ( $\text{CCl}_4$ ).

Chloroform.

Ethyl Ether.

$\beta$ -Naphthol in Sodium Hydroxide (50 g. per l.).

Iodine Solution, containing 0.2 g. of iodine per l. of  $\text{CCl}_4$ .

Petroleum Ether, b.p. 40 to 60°C.

Phenol.

Sodium Hydroxide Solution (50 g. per l.).

Sodium Hydroxide Solution (200 g. per l.).

Sodium Nitrite Solution (18 g.  $\text{NaNO}_2$  per l.).

Zinc, granulated.

*Procedure.*—Confirm the identification of rubber polymer made by pyrolysis products or spot tests by means of the following confirmatory tests:

CR.—Shake a 0.2-g. sample with 2 ml. of iodine solution. If the violet color fades noticeably in 2 to 3 minutes, CR is indicated.

Burn the sample in contact with a clean copper wire. A persistent green flame indicates chlorine.

SBR-NR-IR.—Asphaltic extenders may interfere with distinguishing between SBR and NR or IR by the pyrolysis test.

If 2 ml. of chloroform show an appreciable darkening when shaken with a 0.2-g. sample of vulcanized rubber product, extract a fresh sample with chloroform in



accordance with the section on Chloroform Extract, p 2205, dry the extracted sample in a vacuum oven for 1 hour at 70°C, and repeat the pyrolysis test.

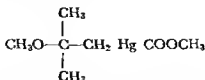
If 2 ml of acetone show an appreciable darkening when shaken with a 0.2 g sample of rubber or unvulcanized rubber product, extract a fresh sample with acetone in accordance with the section on Acetone Extract, page 2156, dry the extracted sample in a vacuum oven for 1 hour at 70°C, and repeat the pyrolysis test.

**NR IR**—Extract a fresh portion of the sample with acetone in accordance with the section on Acetone Extract, page 2156. Place a few milligrams of the extracted sample in a small evaporating dish and swell it in a little  $\text{CCl}_4$ . Add a few drops of bromine and let stand for about 2 minutes. Add about 1 g of phenol and warm on a steam bath to remove the  $\text{CCl}_4$ . A blue to red violet color indicates NR or IR.

**SBR**—Boil 1 to 2 g of dried, acetone extracted sample under reflux with 20 ml of  $\text{HNO}_3$  for 1 hour. Dilute by pouring into 100 ml of water. Extract with 50, 25 and 25 ml portions of ethyl ether. Combine the ether extracts and wash twice with 15 ml portions of water, discarding the water washings. Extract the ether solution with three 15 ml portions of NaOH solution (50 g. per l.) and finally with 20 ml of water. Discard the ether. Combine the caustic extracts and water washing, make just acid with HCl, and add 20 ml in excess. Heat on a steam bath and reduce the nitrobenzoic acid by adding 5 g of granulated zinc. Make the solution alkaline with NaOH solution (200 g per liter), adding sufficient excess to just dissolve the precipitate that forms. Extract twice with ether and discard the ether. Make the aqueous solution acid with HCl, cool to room temperature, and add 2 ml of  $\text{NaNO}_2$  solution. Pour this diazotized solution into an excess of solution of  $\beta$  naphthol in NaOH. A vivid scarlet color indicates SBR.

**IIR**—Destructive distillation of IIR yields a white difficultly condensable vapor. A light yellow mobile oil is obtained.

Place about 1 g of dried, acetone extracted sample in a test tube provided with a stopper and a bent delivery tube passing through a stopper almost to the bottom of a second test tube having a side arm. Cool the second tube with ice. By means of a delivery tube, connect the side arm of the second test tube to a small open test tube containing 0.5 g of mercuric acetate in 10 to 15 ml of methanol. Heat the rubber strongly so that it is virtually all decomposed and distilled off. Discard the liquid that collects in the second test tube. Evaporate the methanol from the third tube but do not heat excessively toward the end of the evaporation. Boil the residue with 25 ml of petroleum ether and filter from insoluble matter. Evaporate the filtrate to a small volume, chill in ice, and scratch the sides of the vessel to induce crystallization. Dry the mercury derivative at 30 to 40°C and determine the melting point (about 55°C). Carry out a mixed melting point determination with the mercury derivative made from known IIR. The derivative is thought to be methoxyisobutyl mercuric acetate,



## IDENTIFICATION OF SYNTHETIC RUBBERS— INFRARED ABSORPTION METHOD

While the infrared absorption method for identification of crude rubbers has not been accepted as a standard method by any standardizing body, it has become by

general usage a method fully as useful as a standard method. Moreover, it has the added advantage of permitting the identification of all types of rubbers and of distinguishing them from plastics or other rubbery materials which may appear to resemble rubbers when examined in the crude state. The disadvantage is the equipment necessary. This is a serious problem only to the small control laboratory. Today, any laboratory which does any considerable amount of work on identification of organic compounds can scarcely do without one of the comparatively inexpensive bench model infrared spectrophotometers. It is probable that the lack of standardization in this field is due to the variety of techniques and instruments available. Two useful methods are outlined below.

*a. Film Transmission Method.*—Obtain the infrared absorption spectrum from about 2.5 to 15 microns on a film of the rubber prepared by pressing the sample, or by dissolving it in a suitable solvent, painting or spreading it on a rock salt plate and evaporating the solvent. Compare the spectrum with reference spectra of the various rubbers. See the section on Identification of Rubber Polymers, page 2191, for references.

*b. Pyrolysis Method.*—Prepare a pyrolyzate of about 0.5 g. of rubber by heating in a test tube as described in the section on Identification of Rubber Polymers. Obtain the infrared absorption spectrum of the pyrolyzate and compare with known spectra prepared in a similar manner.

### COMPOSITION OF THE POLYMER OR COPOLYMER IN A CRUDE RUBBER

The determination of the composition of a crude rubber is of importance for specification purposes and is often of scientific value.

#### *BOUND STYRENE IN SBR*

The most common example of the need for composition analysis is the determination of the bound styrene (copolymerized styrene) content of the general purpose synthetic rubber, SBR, and of the various other copolymers of styrene and butadiene that are commercially available. The ASTM method<sup>s</sup> for this determination is the accepted standard of the industry. It has the disadvantage of being useful only for rubber from which all foreign substances can be extracted. It is obviously not useful for the commercially available mixtures with carbon black, and it is not currently used as a standard method for use with oil-extended crude SBR although it may be so used. The following is a detailed description of the method.

*Summary of Method.*—The thinly dried and sheeted sample is cut in small strips, then extracted twice with ethanol-toluene azeotrope in a 400-ml. flask at the boiling point of the solvent. The extracted rubber is dried, then pressed between sheets of aluminum foil. Strips of the rubber are then pressed against the prism of a refractometer and the index of refraction measured. The percentage of bound styrene is calculated or determined from a table of known values at given refractive index and temperature.

*Apparatus and Materials.* Spiders, consisting of  $\frac{1}{2}$ -in. squares of sheet aluminum or stainless steel, having a Nichrome wire leg about  $1\frac{1}{2}$  in. long attached to each corner; and of  $\frac{1}{2}$ -in. squares cut from a sheet of tantalum, having legs of tantalum wire  $1\frac{1}{2}$  in. long.

<sup>s</sup> Tentative Methods for Chemical Analysis of Synthetic Elastomers (Solid Styrene-Butadiene Copolymers), ASTM Designation: D1416-61T.

Flask 400 ml

Vacuum Oven

Aluminum Foil

Abbe Refractometer, four place

Glass Test Piece standard for checking adjustment of the refractometer

Ethyl Alcohol and Lens Paper, for cleaning the test piece

Flashlight Bulb or Auto Lamp, not exceeding 3 candlepower

Tube of Rolled Aluminum approximately 2 in long

Tissue Paper

Alpha Bromonaphthalene, for pressing between glass test piece and measuring prism of the refractometer

Razor Blade

**Reagents** Ethanol Toluene Azeotrope (ETA), prepared by mixing 70 volumes of ethyl alcohol and 30 volumes of toluene refluxing the mixture 4 hours over CaO and distilling. Discard the first and last portions keeping only that distillate coming over within a range of 1°C. Distilling may be avoided by using absolute grain alcohol or anhydrous Formula 2 B alcohol.

Acidified Ethanol Toluene Azeotrope, made by adding 10 ml of HCl to a portion of the ETA and making up to 1 l with the ETA.

**Procedure**—(a) Dry the polymer in accordance with directions given in the sections on Volatile Matter by the Hot Mill Method or Volatile Matter by the Mill Oven Method pages 2176 and 2177 and sheet it to a thickness of 0.020 in or less. Cut the sheeted polymer into strips approximately  $\frac{1}{4}$  in wide and 1 in long. Fasten one strip to each leg of the aluminum or stainless steel spider thus allowing each portion of rubber to be contacted on all sides by the solvent. Place the spider and strips in the 400 ml flask into which 60 ml of ETA has been placed. For alum coagulated polymers use 60 ml of acidified ETA and the tantalum spiders. Extract for 1 hour at a temperature at which the solvent boils gently replace the solution with another 60 ml of ETA or acidified ETA and extract for another hour (NOTE 1). Remove the spider from the flask and dry the rubber in the vacuum oven at about 100°C for at least 1 hour. Avoid plastication of the sample by overheating.

**NOTE 1**—It is important that the test specimens be extracted and dried thoroughly since either residual solvent or incompletely extracted materials will result in erroneous readings of the refractive index.

(b) After the specimens have been thoroughly dried remove the strips from the spider. Prepare 1 in squares from the clean aluminum foil. Press each strip between two of the aluminum squares with a force of 50 to 300 lb for each specimen (for example if ten squares are pressed at the same time use a force of 500 to 3000 lb) and at a temperature of 100°C for from 3 to 10 minutes. The period of time most suitable for the pressing is that which results in the most distinct line dividing the light and dark portions of the telescope field. Hold the strips at the same pressure for 10 minutes at room temperature either by circulating cold water through the press platens or by using a press equipped with both cold and hot platens.

(c) Measure the refractive index with the Abbe refractometer in the same manner as that used for measuring the index of solids. Check the adjustment of the refractometer using the standard glass test piece (NOTE 2). Circulating water at 25°C through the prism or performing the test in a constant temperature room at

Place the specimen on the prism of the refractometer with the cut edge away from the observer, perpendicular to the length of the prism face, and at the same position occupied by the polished edge of the glass test piece. Press the specimen firmly against the foil until it wets the glass leaving no air entrapped between the prism and the specimen near the cut edge (NOTE 6).

NOTE 6 *Caution*—Under no circumstances should the rubber specimen be clamped between the two refractometer prisms as in measurements with liquids. Attempts to close the prisms with rubber between them may distort the hinges, loosen the prism mountings or damage the prisms.

(f) Circulate water having a temperature within 2°C of room temperature through the tap housing to the measuring prism of the refractometer and through a cored brass block of about the same size as the prism housing, mounted over the specimen. Allow at least 1 minute for the specimen to reach temperature equilibrium after the block has been placed over the specimen and before an index reading is made.

(g) Adjust the compensator to give as nearly white light as possible and set the boundary between the light and dark portions of the field on the intersection of the cross hairs. In reading the line adjust the compensator drum so that of the two possible points of compensation the one used with the rubber specimen is the one nearer to that used with the glass test piece. Approach the setting from a position in which the intersection is in the light portion of the field. Make at least three readings and if there is a difference of more than 0.0001 between the readings mount a new strip on the prism and repeat the readings. If average values obtained on different specimens from the same pressed specimen differ by more than 0.0002 extract a new portion of the original sample and repeat the measurements. At each reading record the temperature to the nearest 0.1°C by means of a thermometer graduated in units of 0.2°C or less.

Calculation—(a) Calculate the value of the refractive index at 25°C from the observations as follows

$$n_{25} = n_t - 0.00037(t - 25)$$

where  $n_{25}$  = refractive index at 25°C, and

$n_t$  = refractive index observed at temperature,  $t$

(b) Calculate the bound styrene as follows

$$S = 23.50 + 1164(n_{25} - 1.53456) - 3497(n_{25} - 1.53456)^2$$

where  $S$  = styrene content of the rubber hydrocarbon in per cent by weight

#### NITROGEN CONTENT OF NBR RUBBERS

The bound acrylonitrile (copolymerized acrylonitrile) content of NBR rubbers is of particular interest in that it determines the oil resistance of the rubber. Nitrogen may be determined by the Kjeldahl methods given in Volume I of *Standard Methods of Chemical Analysis* or in the *Standard Method of Test for Organic Nitrogen in Paper and Paperboard*\*. An abstract of these methods as applied to the determination of nitrogen in NBR rubber is given here.

\* ASTM Designation D982-52

**Apparatus.**—A Kjeldahl digestion and distillation apparatus will be required. Apparatus with ground-glass joints, preferably of the interchangeable type, is desirable. An 800-ml. Kjeldahl flask is a suitable size.

**Reagents.** Sodium Sulfate.—Anhydrous, powdered, c.p.  $\text{Na}_2\text{SO}_4$ .

Cupric Sulfate.—Crystallized, c.p.  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ .

Selenium Oxychloride.—c.p.  $\text{SeOCl}_2$ .

Metallic Mercury or Mercuric Oxide, c.p.

Sulfuric Acid (sp. gr. 1.84).—c.p. concentrated  $\text{H}_2\text{SO}_4$ .

Zinc.—Granulated or stick zinc.

**Sulfide or Thiosulfate Solution.**—Any of the following solutions may be used: 40 g. of commercial  $\text{K}_2\text{S}$  or 40 g. of  $\text{Na}_2\text{S}$  or 80 g. of  $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$  dissolved in 1 liter of distilled water.

**Sodium Hydroxide Solution (785 g. per l.).**—Dissolve 785 g. of c.p.  $\text{NaOH}$  in distilled water and dilute to 1 liter.

**Standard Sulfuric or Hydrochloric Acid (0.1 N).**—Dilute 8.5 ml. of  $\text{HCl}$  (sp. gr. 1.18) or 2.8 ml. of  $\text{H}_2\text{SO}_4$  (sp. gr. 1.84) to 1 liter with distilled water and standardize accurately.

**Alcoholic Methyl Red Indicator Solution.**—Dissolve 1 g. of methyl red indicator in alcohol and dilute to 1 liter.

**Standard Sodium Hydroxide Solution (0.1 N).**—Dissolve 4 g. of c.p.  $\text{NaOH}$  in distilled water and dilute to 1 liter. Standardize against the standard acid, using methyl red indicator.

**Boric Acid Solution (40 g. per l.).**—Dissolve 40 g. of c.p.  $\text{H}_3\text{BO}_3$  in warm distilled water, dilute to 1 liter, and cool to room temperature.

**Alcoholic Mixed Indicator Solution.**—Dissolve 4 g. of bromcresol green and 0.8 g. of methyl red in alcohol and dilute to 1 liter.

**Procedure.**—Place about 0.5 g. of the prepared specimen, weighed to the nearest 1 mg., in the Kjeldahl flask. Add 10 g. of powdered, anhydrous  $\text{Na}_2\text{SO}_4$  and either 0.3 g. of crystallized  $\text{CuSO}_4$  or 0.15 g. (5 drops) of  $\text{SeOCl}_2$  solution, and about 0.5 g. of metallic mercury or 0.55 g. of  $\text{HgO}$ . Then add 25 ml. of  $\text{H}_2\text{SO}_4$  (sp. gr. 1.84). Place a small glass funnel or a Tuttle flask cover in the neck of the flask, heat gently under a hood over a flame until frothing has ceased, and then digest with increasing temperature until oxidation is complete. This generally requires 1 to 2 hours after the mixture becomes clear and colorless, or nearly so.

Cool and dilute with 300 to 325 ml. of water. Add about 2 g. of stick or granulated zinc to prevent bumping during the distillation (the stick zinc may be used for several distillations) and 25 ml. of the sulfide or thiosulfate solution. (When  $\text{Na}_2\text{S}_2\text{O}_3$  is to be used, mix it first with the  $\text{NaOH}$  solution so that they may be added together.) Add  $\text{NaOH}$  solution (785 g. per l.) to the contents of the flask in such amount (usually 55 ml.) that there is an excess of 5 ml. present. This solution must be poured carefully down the side of the flask so that it does not mix with the acid contents. The total volume of the solution should be about 400 ml.

Immediately connect the flask to a condenser having the discharge end of its delivery tube just beneath the surface of a measured amount of 0.1 N  $\text{H}_2\text{SO}_4$  or  $\text{HCl}$  diluted to 100 ml. (25 ml. of 0.1 N acid is usually sufficient), or just beneath the surface of 100 ml. of  $\text{H}_3\text{BO}_3$  solution (40 g. per l.). Mix the contents of the Kjeldahl flask by swirling the flask, slowly at first and then more rapidly. Start heating the flask immediately and distill the contents for about 45 minutes, taking care to avoid spurting. The total volume of distillate should be about 200 ml.

Titrate the contents of the receiver flask with 0.1 N NaOH, using methyl red indicator (when  $\text{H}_2\text{SO}_4$  or HCl is used as the receiving solution), or with 0.1 N  $\text{H}_2\text{SO}_4$  or HCl, using mixed bromocresol green-methyl red indicator (when  $\text{H}_3\text{BO}_3$  is used as the receiving solution)

**Blank**—Make a blank determination by conducting the entire procedure, using only the reagents

**Calculation**—When  $\text{H}_2\text{SO}_4$  or HCl is used as the receiving solution calculate the nitrogen content as follows

$$\text{Nitrogen, per cent} = \frac{(V_2 - V_1) \times N \times 0.014}{W} \times 100$$

where  $V_1$  = milliliters of NaOH solution required to titrate the contents of the receiver flask,

$V_2$  = milliliters of NaOH solution required to titrate the contents of the receiver flask in the blank

$N$  = normality of the NaOH solution, and

$W$  = grams of test specimen

When  $\text{H}_3\text{BO}_3$  is used as the receiving solution calculate the nitrogen content as follows

$$\text{Nitrogen, per cent} = \frac{(V_1 - V_2) \times N \times 0.014}{W} \times 100$$

where  $V_1$  = milliliters of acid required to titrate the distillate from the determination,

$V_2$  = milliliters of acid required to titrate the distillate from the blank

$N$  = normality of the acid solution and

$W$  = grams of test specimen

### CHLORINE CONTENT OF CR RUBBERS

The chlorine content of crude polychloroprene (CR) or of copolymers with chloroprene may be determined by the Standard Method of Test for Total Chlorine in Vinyl Chloride Polymers and Copolymers<sup>10</sup> if the details of the method abstracted below are followed. The method can also be applied to vulcanized CR samples and to other chlorine containing polymers and copolymers. For use with this method the specimen not exceeding 0.225 g must be as finely divided as possible and must be added to the sodium peroxide in the bomb cup in such a manner as to prevent aggregation of the particles of the specimen. The nominal value of the chlorine content of crude commercial CR is considered to be 37 per cent.

**Outline of Method**—The organic matter is destroyed by hot sodium peroxide and the chlorine is converted to chloride. The chloride is precipitated as silver chloride with an excess of standard silver nitrate, and this excess is determined by titration with standard thiocyanate solution using ferric nitrate indicator and nitrobenzene to depress the solubility of the silver chloride. The amount of silver nitrate required to precipitate the chloride is a measure of the total chlorine content of the sample.

**Apparatus** Parr Peroxide Bomb, Series 2100, 22 ml, gas fired. (The Parr Peroxide Bomb may be obtained from the Parr Instrument Co., Moline Ill.)

*Reagents and Materials.* Powdered Sugar (preferably c.p. sucrose).

Sodium Peroxide, c.p., calorific grade, assay 95%, minimum, as  $\text{Na}_2\text{O}_2$ . (Keep  $\text{Na}_2\text{O}_2$  in a tightly closed container, and away from moisture.)

Nitric Acid (sp. gr. 1.42).

Silver Nitrate Solution (0.1 N).

Ammonium or Potassium Thiocyanate Solution (0.1 N).

Ferric Nitrate Solution (50 g.  $\text{Fe}(\text{NO}_3)_3$  per l).

Nitrobenzene, c.p.

*Procedure.*—To a clean, dry, 22-ml. Parr bomb cup add 0.200 to 0.225 g. of finely divided sample. Add 0.5 g. of dry powdered sugar and a standard measure (15 g.) of  $\text{Na}_2\text{O}_2$ . Close the bomb tightly with the lid and the retaining rings, and shake vigorously to mix the contents. Tap the bomb lightly on the bench to dislodge particles sticking to the cap and to the upper portion of the bomb cup. Set the bomb over the hole in a steel housing supported on a tripod. A small steel chamber with an access door and a small sight hole built over the tripod is desirable for reasons of safety.

Add 2 ml. of water to the depression in the bomb cover. Apply a very hot Bunsen flame to the bottom of the bomb. Adjust the air to the burner to give a cone about  $1\frac{1}{2}$  in. high, the apex of which should be just short of contact with the bottom of the bomb. Allow to heat until the water in the lid begins to boil or until a dark red ring appears on the side of the cup, then quench in cold water. *Caution:* The heating of the bomb is of extreme importance, since underheating will cause incomplete oxidation of the organic matter and low chlorine results, while overheating will cause possible damage to the bomb cup and even an explosion. These bombs are not intended to operate at a red heat, but there is no serious danger involved in this method of oxidation provided the proper charges are used in a bomb that is in a satisfactory condition, and provided the proper heating technique is used (NOTE 1). The 22-ml. bomb cups should be discarded if the sides or bottom become visibly swollen, or if the interior surfaces become worn or corroded to an inside diameter of 1.08 in. at any point.

When the bomb is cold, remove it from the quenching bath, rinse it off with water, and open. Place the bomb cup on its side in a clean 600-ml. beaker and add water until about half covered. Rinse off the bomb cover thoroughly with water, catching the rinsings in the same beaker. Cover the beaker with a watch glass, and warm slightly until the contents of the bomb are dissolved. Remove the bomb cup and rinse thoroughly with water, catching the rinsings in the same beaker. Transfer quantitatively to a 500-ml. glass-stoppered flask, add 2 to 3 drops of phenolphthalein indicator, neutralize with  $\text{HNO}_3$ , using care to avoid loss by spattering and overheating, and add an excess of 5 ml. of  $\text{HNO}_3$  (NOTE 2). Add 2 ml. of nitrobenzene (NOTE 3) and 50.0 ml. of 0.1 N  $\text{AgNO}_3$  solution, stopper, and shake until the precipitated  $\text{AgCl}$  becomes a spongy mass. Add 10 to 15 ml. of  $\text{Fe}(\text{NO}_3)_3$  indicator solution and titrate with 0.1 N thiocyanate solution to the first pink end point.

Run a blank determination at least every time a change in solutions or reagents is made, to insure against high results caused by chlorides in the reagents.

NOTE 1.—A careful reading of Parr Manual No. 121 on the method and precautions used in this method is suggested.

NOTE 2.—When properly fired, the bomb leachings are free of black particles, and the acidified solution is substantially clear. If not, a new sample must be prepared and fired.

NOTE 3 *Caut on*—Nitrobenzene is toxic and care must be used to avoid contact with the skin

**Calculations**—Calculate the chlorine content as follows

$$\text{Total chlorine per cent} = \frac{(\text{ml of } \Lambda \text{ Ag NO}_3 - \text{ml of } \Lambda \text{ thiocyanate}) \times 3.546}{\text{wt of sample}}$$

### OTHER SYNTHETIC RUBBERS

No standard methods or published methods that have attained wide usage exist for the determination of the polymer or copolymer content of other crude synthetic rubbers with the exception of IR the polyisoprene content of which may be determined by the method given in the section Isoprene Polymer (NR or IR) page 2161. Certain special purpose rubbers can undoubtedly be analyzed by specific functional group methods.

Infrared absorption rather than chemical methods will in all probability become the standard methods of the future for the analysis of many of the newer rubbers based on polymers of diolefins and olefins particularly those containing specific structural configurations. The simplicity of this technique as used on pressed films or films spread from solution commends it as a standard method. Unfortunately variations in equipment variations in current methods of pressing spectra in publications and the high degree of skill necessary to interpret minute differences in the spectra as well as differences arising from the degree of crystallinity of the polymers make this technique a research tool rather than one for routine use in determination of polymer structure. It is however the best available procedure for the determination of general composition of most polymers and copolymers when sufficient calibration data have been obtained. Its use both for composition and structure determination cannot be overemphasized in view of the fact that the properties of these rubbers are usually dependent on their composition and structure.

### DETERMINATION OF NONRUBBER CONSTITUENTS IN SBR

The methods applicable to SBR have been worked out and have been adopted as Tentative Standards by the ASTM.<sup>8</sup> These methods may be applied to other synthetic rubbers in cases where it can be proved that they will yield satisfactory results. The details of the procedures are given below.

#### VOLATILE MATTER BY THE HOT MILL METHOD

**Scope and Application**—Reference to volatile matter pertains principally to the moisture content of the elastomer. A situation may arise where the polymer is too sticky to handle satisfactorily on a hot mill. If such is the case the Mill O.C. Method which follows should be used.

**Summary of Method**—A weighed sample of rubber is sheeted out on a heated mill until all volatile matter is driven off. A sample is weighed again and the percentage of volatile matter is calculated.

**Procedure**—Weigh the representative sample (at least 450 g) to the nearest 0.1 g. Pass the weighed sample repeatedly through a laboratory mill with the rolls of the mill maintained at 200 to 220 F and the distance between the rolls at  $0.010 \pm 0.002$  in as determined by a lead slug. Do not allow the sample to band and take care to prevent any loss of sample. At the end of 4 minutes weigh the sample.



to the nearest 0.1 g. Pass the sample through the mill for an additional 2 minutes, and reweigh it. If the weights at the end of the 4- and 6-minute periods are within 0.1 g., calculate the volatile matter; if not, continue passing the sample through the mill for 2-minute periods until the weight remains constant within 0.1 g.

**Calculation.**—Calculate the percentage of volatile matter as follows:

$$\text{Volatile matter, per cent} = \frac{A - B}{A} \times 100$$

where  $A$  = weight in grams of the original sample, and

$B$  = weight in grams of the sample after milling.

#### *VOLATILE MATTER BY THE MILL-OVEN METHOD*

**Scope and Application.**—This method is used principally to determine the moisture content of solid synthetic elastomers that are normally too tacky to be handled satisfactorily on a heated mill.

**Summary of Method.**—A weighed sample of polymer is sheeted out on a laboratory mill, then placed in an oven and dried to constant weight. The difference in weight before and after drying is calculated as volatile matter.

**Procedure.**—Sheet out the sample of the polymer (at least 250 g.) on a laboratory mill, with the distance between the rolls set at  $0.010 \pm 0.002$  in. as determined by a lead slug, and the temperature of the roll being no greater than 90°F. Weigh the entire sheet to the nearest 0.1 g. Place in a forced-circulation oven set at 200 to 220°F. so that both surfaces of the sheet are exposed to the draft. Allow the sample to remain in the oven until the weight is constant to within 0.1 g. Usually 1 hour is sufficient for polymers containing no more than 1.0% moisture.

**Calculation.**—Calculate the percentage volatile matter as follows:

$$\text{Volatile matter, per cent} = \frac{A - B}{A} \times 100$$

where  $A$  = weight in g. of the sample before placing in the oven, and

$B$  = weight in g. of the sample after drying.

#### *TOTAL ASH*

**Summary of Method.**—The dried sample is accurately weighed into a tared crucible and ignited in a muffle furnace at about 550°C. until all the carbonaceous material is oxidized. The crucible is then allowed to cool in a desiccator, weighed, and the percentage of ash is calculated.

**Apparatus.** Crucible, tared, having a minimum volume of 25 ml. per g. of sample; or an aluminum dish of 50-ml. volume.

If water-soluble ash is to be determined (see method following), use a fine-porosity fritted-glass filtering crucible, placing a small ashless filter paper in the bottom of the crucible in order to prevent loss of liquid pyrolysis products.

Ashless Filter Paper, 15 cm. in diameter.

Muffle Furnace, with suitable temperature control.

**Preparation of Sample.**—Prepare the sample by drying, in accordance with directions given in sections on Volatile Matter by the Hot-Mill Method or Volatile Matter by the Mill-Oven Method, above, and sheet it to a thickness of 0.020 in. or less.

**Procedure**—Accurately weigh 3 to 5 g of the dried and sheeted sample in the tared crucible, which has been ignited to constant weight at  $550 \pm 25^\circ\text{C}$ . In the case of alum coagulated rubbers which tend to boil over during ashing wrap the sample tightly in a 15 cm ashless filter paper before ashing. Place the crucible containing the sample directly into the muffle furnace at  $550 \pm 25^\circ\text{C}$  and allow it to remain there until the carbonaceous material in the sample has been completely oxidized.

**Caution**—Do not open the door of the furnace for at least 1 hour after the crucible has been placed in the furnace.

After the carbon has been completely oxidized remove the crucible from the furnace, cool it to room temperature in the desiccator, and weigh it. If the ash line is less than  $\frac{1}{8}$  in. below the rim of the crucible discard the sample and determine the ash content of an alternate sample.

Save the ashed sample if soluble ash is to be determined.

**Calculation**—Calculate the percentage of total ash as follows

$$\text{Total ash, per cent} = \frac{F - E}{D - E} \times 100$$

where  $D$  = weight in g of the crucible plus the dry sample,

$E$  = weight in g of the crucible, and

$F$  = weight in g of the crucible plus the ash

#### WATER SOLUBLE ASH

**Summary of Method**—The ash obtained in determining total ash in the foregoing procedure is digested and washed with three 30 ml portions of water the crucible and contents are dried in an oven, and the crucible is then placed in a muffle furnace to oxidize the carbonaceous material. The crucible is then cooled weighed and the percentage of soluble ash is calculated.

**Apparatus** Filtering Crucible, of fine porosity fritted glass or a sintered porcelain crucible

Ashless Filter Paper, small

Glass Stirring Rod

Rubber Policeman, diagonal form

Drying Oven

Muffle Furnace, equipped with a suitable temperature control

**Procedure**—Ash the sample as described in the foregoing procedure for total ash determination using a filtering crucible having a fine porosity, fritted glass bottom, and containing the small ashless filter paper in the bottom. Add 30 ml of hot water at a temperature of 80 to  $90^\circ\text{C}$ , to the crucible. Allow to stand for 5 minutes stirring with the glass rod having the rubber policeman. Filter the solution with suction and repeat the digestion with two additional 30 ml portions of hot water. Place the crucible in the drying oven at  $105 \pm 5^\circ\text{C}$  for 1 hour. Then place the crucible in the muffle furnace at  $275 \pm 25^\circ\text{C}$  and allow it to remain until all the carbonaceous material has been completely oxidized. If the sintered porcelain crucible is used, heat in the furnace at  $550 \pm 25^\circ\text{C}$ . (**Caution** Do not open door of furnace for at least 1 hour after crucible has been placed in it.)

After the carbon has been completely oxidized, remove the crucible from the muffle furnace, allow it to cool to room temperature in a desiccator, and accurately weigh it.

Calculation.—Calculate the percentage of water-soluble ash as follows:

$$\text{Water-soluble ash, per cent} = \frac{(F - G)}{D - E} \times 100$$

where  $D$  = weight in g. of the crucible plus the dry sample,

$E$  = weight in g. of the crucible,

$F$  = weight in g. of the crucible plus the total ash, and

$G$  = weight in g. of the crucible plus the insoluble ash.

### CARBON BLACK IN MASTERBATCH

**Summary of Method.**—The prepared dried sample and a sample of standard SBR (GR-S) black determinate<sup>11</sup> are tested in triplicate. The samples are accurately weighed into tared crucibles, and then placed in a combustion tube, at 550°C., which is continuously flushed with CO<sub>2</sub> until the rubber hydrocarbon is distilled. The crucibles and contents are cooled in a desiccator, weighed, then inserted into a muffle furnace at 550°C. until all carbonaceous material is burned. The crucible and contents are again cooled in a desiccator and weighed. The percentage of carbon black is calculated from the weights.

#### **Apparatus. Drying Oven.**

Six Porcelain Crucibles, No. 00000, tared.

Weighing Bottles, tared.

Fused Alumina Combustion Boats.<sup>12</sup>

Combustion Tubes.<sup>13</sup>

Combustion Furnace.

**Preparation of Sample.**—Blend 200 g. of the dried sample obtained in accordance with directions in sections on Volatile Matter by Hot-Mill or Mill-Oven Methods, pages 2176 and 2177, by passing it five times between the rolls of a laboratory mill. Maintain the roll temperature at  $120 \pm 10^\circ\text{F.}$  and a distance between the rolls of  $0.020 \pm 0.005$  in. After blending, sheet the sample from the mill with the distance between the rolls set at  $0.010 \pm 0.002$  in. Dry approximately 2 g. of the blended, thinly sheeted material for 1 hour in the oven at 200 to 220°F. Keep the dried sheet in a desiccator until ready to weigh the samples.

**Procedure.**—Into the tared porcelain crucibles accurately weigh three 0.3- to 0.5-g. samples from the sheet of material being tested and three 0.3- to 0.5-g. samples from a similarly prepared sheet of standard GR-S black determinate. Due to the hygroscopic nature of the samples and the carbon black, weigh the crucibles and contents in the tared weighing bottles.

Place the six crucibles in a fused alumina combustion boat, or boats, alternating the samples of determinate and the test samples. Insert the combustion boat, or boats, into the combustion tube. Pass a stream of oxygen-free CO<sub>2</sub> through the tube, at a flow-rate of 150 to 250 ml. (atmospheric pressure) per minute. After the tube has been swept free of oxygen (approximately 5 minutes is sufficient time),

<sup>11</sup> Standard SBR black determinate may be prepared by careful mill mixing of the particular type of carbon black being determined with SBR on a laboratory mill. The weight of carbon black used and the total batch weight determine the percentage of black in the determinate, on an as-compounded basis.

<sup>12</sup> Alundum No. 3 combustion boats have been found satisfactory for this purpose.

<sup>13</sup> The McDaniel high-temperature combustion tube, 30 in. long by 1 in. in diameter, or equivalent, is recommended. This tube will accommodate a maximum of two combustion boats containing six samples each within the heated area of the furnace.

## ORGANIC ACID

**Summary of Method.**—Thin narrow strips of the dry polymer are accurately weighed to secure about 6 g. The strips are extracted twice with hot ethanol-toluene azeotrope (ETA) solvent for 1 hr. each. The solvent used in the extraction is transferred to a 250-ml. volumetric flask. The sample strips are rinsed with three successive 10-ml. portions of ETA. The rinsings are then transferred to the volumetric flask, and the total volume brought to 250.0 ml. A 100-ml. portion is titrated to the first color change with 0.1 N NaOH, using meta-cresol-purple as indicator. The titration and weighings are used to calculate the organic acid.

**Apparatus.** Wide-Mouth Flask, 400- to 550-ml.

Volumetric Flask, 250-ml.

Hot Plate.

Pipet, 100-ml.

Erlenmeyer Flasks, 250-ml.

Graduated Pipet, 25-ml.

**Reagents.** Ethanol-Toluene Azeotrope (ETA).—See preparation of this reagent in Method for Bound Styrene in SBR, page 2169. When testing alum-coagulated polymers, add 5 ml. of water to 95 ml. of anhydrous ETA.

Meta-Cresol-Purple Indicator Solution (0.1%), in ethyl alcohol or in water. Neutralize each 0.1-g. of indicator with 26.2 ml. of 0.01 N NaOH solution.

Standard Sodium Hydroxide Solution (0.10 N).

**Preparation of Sample.**—Dry the polymer in accordance with directions in sections on Volatile Matter by Hot-Mill or Mill-Oven Methods, pages 2176 and 2177, and sheet it to a thickness of 0.020 in. or less. Cut approximately 6 g. of the dried, sheeted material into strips not wider than 1 cm. nor longer than 5 cm.

**Caution.**—Be sure the strips are less than 0.020 in. thick in order to secure complete extraction.

**Procedure.**—Accurately weigh a 6-g. sample of the dried strips. Add 100 ml. of ETA to the 400- to 550-ml. flask. Add each strip in the weighed sample separately to the flask, swirling the flask after each addition so that each strip is thoroughly wetted with the solvent to avoid sticking. To prevent the sample from sticking to the flask, place a filter paper in the bottom of the flask or use a wire gauze or asbestos mat between the flask and the hot plate. Reflux the contents of the flask on the hot plate for 1 hour.

Decant the liquid into a 250-ml. volumetric flask. Add a second 100-ml. portion of the ETA to the polymer sample and reflux again for 1 hour. Decant the liquid into the volumetric flask. Rinse the sample with three successive 10-ml. portions of fresh ETA and add these rinsings to the volumetric flask. Cool the ETA solution to room temperature and add enough fresh ETA to bring the volume to 250.0 ml. Mix the contents thoroughly.

Measure with a pipet, two 100-ml. portions of the ETA solution into 250-ml. Erlenmeyer flasks. Save one 100-ml. portion for the soap determination, which follows this method.

To one 100-ml. portion of ETA solution, add 6 drops of meta-cresol-purple indicator solution. Titrate the ETA solution with 0.1 N NaOH to the first color change. Run a blank titration, using 100 ml. of fresh ETA that has been treated in the same manner as the sample, and using the same indicator. Deduct the volume of NaOH solution used for the blank from that used for the titration.

Calculation—Calculate the percentage of organic acid as follows

$$\text{Organic acid per cent} = \frac{J \times A \times L \times 2.5}{A}$$

where  $A$  = weight in g. of the original dry sample,

$J$  = ml. of NaOH solution used for the titration (corrected for the blank),

$A$  = normality of the NaOH solution, and

$L$  =  $\begin{cases} 28.4 & \text{when organic acid is determined as stearic acid,} \\ 34.6 & \text{when organic acid is determined as rosin acid and} \\ 31.5 & \text{when organic acid is determined as a 50:50 mixture of stearic and} \\ & \text{rosin acid} \end{cases}$

### SOAP

**Summary of Method**—One hundred ml. of the solvent extract remaining from the organic acid test described in the preceding section is titrated with 0.05 N HCl using meta-cresol purple as indicator to the first color change. From the weight of the original sample strips and the titrations the percentage of soap is calculated.

**Reagents**—Standard Hydrochloric Acid Solution (0.05 N)

**Indicator**—One of the following solutions

(1) *Meta Cresol Purple Indicator Solution* (0.1%) prepared in accordance with directions given for that reagent in preceding test for Organic Acid page 2181

(2) *Bromphenol Blue Indicator Solution* (0.1%) in ethyl alcohol

**Preparation of Sample**—Prepare the sample in accordance with the directions given in the preceding test for Organic Acid page 2181 and determine the percentage of soap on the ethanol-toluene azeotrope (ETA) solvent extract remaining from the test for Organic Acid. (See that procedure)

**Procedure**—Add 6 drops of the prepared meta-cresol purple solution to the 100-ml. portion of ETA extract saved from the organic acid test. (See that procedure) Titrate this solution with 0.05 N HCl to the first change in color. Run a blank titration using 100 ml. of fresh ETA that has been treated in the same manner as the sample and using the same amount of indicator. Deduct the volume of HCl solution used for the blank from that used for the titration.

**NOTE**—Some analysts prefer the use of bromphenol blue indicator particularly when testing alum-coagulated polymers and oil-masterbatch polymers.

Calculation—Calculate the percentage of soap as follows

$$\text{Soap, per cent} = \frac{M \times V \times P \times 2.5}{A}$$

where  $A$  = weight in g. of the original dry sample,

$M$  = ml. of standard HCl used for titration (corrected for the blank),

$V$  = normality of the standard HCl solution, and

$P$  =  $\begin{cases} 30.6 & \text{when the soap is determined as sodium stearate,} \\ 36.8 & \text{when the soap is determined as sodium rosinate,} \\ 35.3 & \text{when the soap is to be determined as a 50:50 mixture of potassium} \\ & \text{stearate and potassium rosinate,} \\ 34.5 & \text{when the soap is to be determined as a 50:50 mixture of sodium stea} \\ & \text{rate and potassium rosinate, and} \\ 33.7 & \text{when the soap is to be determined as a 50:50 mixture of sodium stea} \\ & \text{rate and sodium rosinate} \end{cases}$

*ANTIOXIDANT*

**Scope.**—Several antioxidants or stabilizers are used in synthetic rubbers. Four widely used antioxidants are phenyl-beta-naphthylamine, acetone diphenylamine reaction product, mixed alkylated diphenylamines and mixed alkylated phenols. The test procedures for these as submitted here have been in general use by the synthetic rubber producing industry for many years. There are three acceptable methods of analysis. All are described.

**NOTE 1.**—Phenyl-beta-naphthylamine, acetone diphenylamine reaction product, and mixed alkylated diphenylamines are commonly referred to as "PBNA," "BLE," and "Stalite," respectively.

*Method A. Ultraviolet Absorption of Rubber Solution.*

**Summary of Method.**—A dried and weighed sample is dissolved in a suitable spectroscopic solvent and diluted to exactly 250 ml. in a volumetric flask; the absorbance of the solution is determined with an ultraviolet photoelectric spectrophotometer; and the antioxidant content is calculated therefrom. The method is not applicable to mixed alkylated phenols.

**NOTE 2.**—For definitions of terms used in this procedure, refer to the Definitions of Terms and Symbols Relating to Absorption Spectroscopy (ASTM Designation: E131).<sup>14</sup>

**Apparatus.** Volumetric Flask, 250-ml.

Ultraviolet Photoelectric Spectrophotometer.<sup>15</sup>

**Reagents.** Spectroscopic Solvent, having an optical transmission greater than 90%, or, in the case of toluene, greater than 80%, at the wavelength specified for the antioxidant to be determined, as shown in Table 43-5.

**Preparation of Sample.**—Prepare the sample by drying in accordance with directions in Sections on Volatile Matter by Hot-Mill or Mill-Oven Methods, pages 2176 and 2177. Sheet it to a thickness of 0.020 in. or less and cut it into small pieces. Accurately weigh portions of the sample estimated to contain 1.5 to 2 mg. of phenyl-beta-naphthylamine or acetone diphenylamine reaction product, or 2 to 2.5 mg. of mixed alkylated diphenylamines.

**Determination of Absorptivity.**—Determine the absorptivity,  $a$ , (the ratio of the absorbance of a solution 1 cm. thick and the concentration in grams per liter of the solution that is measured), as directed in the following two paragraphs.

Obtain two or more representative samples of the antioxidant, which must, in the case of acetone diphenylamine reaction product and mixed alkylated diphenylamines, be heated to a temperature at which they can easily flow. Thoroughly mix the antioxidant and prepare a standard solution of it in the proper spectroscopic solvent. The concentrations in grams per liter shall be as follows: 0.24 for phenyl beta-naphthylamine or acetone diphenylamine reaction product, and 0.32 for mixed alkylated diphenylamines. Then accurately measure three 3.00-ml. aliquots of this solution into clean 100-ml. volumetric flasks (NOTE 3).

**NOTE 3. Caution.**—It is imperative that clean glassware be used throughout this procedure.

Dilute the solution to 100-ml. with the spectroscopic solvent. Mix each solution thoroughly. Determine the absorbances of these solutions at the appropriate wave-

<sup>14</sup> 1961 Book of ASTM Standards, Part 7.

<sup>15</sup> The Beckman quartz ultraviolet photoelectric spectrophotometer, Model DU, or the equivalent, has been found satisfactory for the purpose.

TABLE 43-5 SOLVENTS AND TEST CONDITIONS FOR DETERMINATION OF ANTIOXIDANT

Polymer	Antioxidant	Spectroscopic Solvent	Wavelength m $\mu$	Background Correct on per Gram of Sample per 250 ml
SBR (GR S)—(hot nonpigmented)	phenyl beta naphthyl amine acetone diphenylamine reaction product	toluene	309 $\pm$ 1	0.085
		methylcyclohexane	309 $\pm$ 1	0.115
		85 per cent methylcyclo- hexane 15 per cent eth- anol <sup>a</sup>	288 $\pm$ 1	0.235
	mixed alkylated diphenyl amines	methylcyclohexane	288 $\pm$ 1	0.225
		85 per cent methylcyclohex- ane 15 per cent ethanol <sup>a</sup>	288 $\pm$ 1	0.235
SBR (GR S)— (cold nonpig- mented)	phenyl beta naphthyl amine acetone diphenylamine reaction product	toluene	309 $\pm$ 1	0.280
		methylcyclohexane	309 $\pm$ 1	0.325
		85 per cent methylcyclohex- ane 15 per cent ethanol <sup>a</sup>	288 $\pm$ 1	0.495
	mixed alkylated diphen- ylamines	methylcyclohexane	288 $\pm$ 1	0.495
		85 per cent methylcyclohex- ane 15 per cent ethanol <sup>a</sup>	288 $\pm$ 1	0.495

<sup>a</sup> Use anhydrous ethyl alcohol.

length as shown in Table 43-5, using the solvent as the blank. Make several measurements on each diluted aliquot until a reproducible result is obtained. Calculate the absorptivity,  $a$ , from this result as follows:

$$a = \frac{100A}{YZ}$$

where  $A$  = measured absorbance (average of three determinations),

$Y$  = concentration of the antioxidant in the standard as grams per liter, and

$Z$  = volume of the aliquot, in milliliters, taken from the standard solution.

**Procedure**—Dissolve the dried sample in 200 ml of the specified spectroscopic solvent contained in a 250 ml volumetric flask, effecting solution by gentle heat if necessary. After the sample has been dissolved and the solution is at room temperature, dilute the solution to 250 ml with the specified solvent and mix the solution thoroughly.

With the spectrophotometer using 1 cm matched quartz cells measure the absorbance of the solution compared to the same spectroscopic solvent used as a blank. If the absorbance is not between 0.4 and 1.0, take a larger sample or dilute the solution, as the case may be, to bring it within this range, and adjust the calculation accordingly.

**Calculation**—Calculate the percentage of antioxidant as follows:

$$\text{Antioxidant, per cent} = 25 \frac{(A - B)}{W_a}$$

where  $A$  = measured absorbance,

$B$  = correction for background absorption of polymer,

$W$  = weight in grams of the original dry sample, and

$a$  = absorptivity

**Method B. Ultraviolet Absorption of Rubber Extract.**

**Summary of Method.**—The weighed sample is extracted with ethanol-toluene azeotrope (ETA) solvent. The total extract is made up to 250 ml. in a volumetric flask and 2 ml. of this extract is diluted to 100 ml. in a volumetric flask with a specified spectroscopic solvent. The absorbance of the diluted extract is determined with an ultraviolet spectrophotometer, and the antioxidant content calculated therefrom. (See NOTE 2). The method is not applicable to mixed alkylated phenols.

**Apparatus.** Volumetric Flask, 100-ml.

Pipet, 2-ml.

Ultraviolet Photoelectric Spectrophotometer.

**Reagents.**—See Method A.

**Preparation of Sample.**—Prepare the rubber extract in accordance with the procedure for Organic Acid, page 2181. Accurately pipet 2 ml. of the ETA extract into the 100-ml. volumetric flask, and dilute to 100.0 ml. with the spectroscopic solvent specified in Method A.

**Procedure.**—With an ultraviolet photoelectric spectrophotometer using 1-cm. matched quartz cells, measure the absorbance of the solution at the wavelength specified in Table 43-5 for the antioxidant to be determined. Prepare the blank by mixing together the spectroscopic solvent and the ETA in the same ratio as that used in the solution containing the ETA extract of the rubber. If the absorbance of the solution containing the antioxidant is not between 0.4 and 1.0, take a different aliquot of the ETA extract so as to bring the absorbance within the desired range, being sure to use the same proportion of ETA in the blank as in the sample.

**Calculation.**—Calculate the percentage of antioxidant as follows:

$$\text{Antioxidant, per cent} = \frac{2500A}{WVa}$$

where  $A$  = measured absorbance,

$W$  = weight in g. of the original sample used for the ETA extract in method for Organic Acid, page 2181.

$V$  = milliliters of ETA extract dissolved in the spectroscopic solvent, and

$a$  = absorptivity (see Method A, page 2183).

**Method C. Mixed Alkylated Phenols.**

**Scope and Application.**—This method is an ultraviolet absorption technique, which is applicable to rubbers made with carbamate shortstop but it is not applicable to oil-masterbatch rubbers. Interference from carbamate shortstop is reduced by using an ethanol-toluene azeotrope (ETA) extract of the rubber rather than a complete solution of the rubber. The high absorbance of oil, at the wavelengths used in this method, masks the measurement of the mixed alkylated phenols absorption.

The difference between the basic and neutral absorbance at 301  $m\mu$  is proportional to the concentration of the mixed alkylated phenols. The neutral absorbance measurement is a background correction for substances other than the active ingredients.

**Summary of Method.**—Two aliquots of the ETA extract are taken. One is left neutral, while the other is made 0.1  $N$  in base with alcoholic potassium hydroxide. The absorbance of both solutions is measured at 301  $m\mu$ , compared to correspond-



ing reference solutions. The difference between the basic and neutral absorptivities is proportional to the concentration of the mixed alkylated phenols.

*Apparatus* Ultraviolet Spectrophotometer<sup>15</sup>

Absorption Cells 1 cm. matched quartz

*Reagents* Ethanol, anhydrous conforming to Formula 2B of the U. S. Bureau of Internal Revenue

Ethanol Toluene Azeotrope (ETA)—See preparation of this reagent in Method for Bound Styrene in SBR, page 2169

Potassium Hydroxide Standard Alcoholic Solution (0.5 N)—Grind 14 g. of potassium hydroxide (KOH) with successive 50 ml. portions of anhydrous ethanol until dissolution is complete. Dilute to 400 ml. with anhydrous ethanol. Filter immediately into a dark bottle and keep tightly closed. Let this solution stand overnight before using. When it becomes noticeably discolored, it should be discarded. Storing in a nitrogen atmosphere will preserve the solution considerably.

*Reference Standards and Calibration*—The spectrophotometric measurements shall be made the same day as the standards are prepared. The slit width of the spectrophotometer should be not more than 0.5 mm. The mixed alkylated phenol used as a standard should be from the same lot of material that is present in the sample being tested.

Prepare a solution of 0.300 g. of mixed alkylated phenols (MAP) in 1 liter of anhydrous ethanol (ethanol MAP solution).

Prepare the basic and neutral standard solutions in two separate 50 ml. volumetric flasks as follows:

#### *Basic Standard Solution*

5 ml. ethanol MAP solution

5 ml. ETA solvent

10 ml. 0.5 N KOH solution

Dilute to mark with ethanol

#### *Neutral Standard Solution*

5 ml. ethanol MAP solution

5 ml. ETA solvent

Dilute to mark with ethanol

Prepare the corresponding reference solutions as follows:

#### *Basic Reference Solution*

5 ml. ETA solvent

10 ml. 0.5 N KOH solution

Dilute to mark with ethanol

#### *Neutral Reference Solution*

5 ml. ETA solvent

Dilute to mark with ethanol

Measure the absorbance of each solution at 301 m $\mu$  using the corresponding reference solution in the spectrophotometer reference cell in each case. Call the observed absorbance values  $A_{\text{basic standard}}$  and  $A_{\text{neutral standard}}$  respectively. Calculate the difference in absorptivity ( $a_{\text{basic}} - a_{\text{neutral}}$ ) as follows:

$$a_{\text{basic}} - a_{\text{neutral}} = \frac{A_{\text{basic standard}} - A_{\text{neutral standard}}}{0.030}$$

where  $a_{\text{basic}}$  = calculated absorptivity of basic solution,  
 $a_{\text{neutral}}$  = calculated absorptivity of neutral solution,  
 $A_{\text{basic standard}}$  = measured absorbance of basic solution, and  
 $A_{\text{neutral standard}}$  = measured absorbance of neutral solution.

**Preparation of Sample.**—Prepare the rubber sample in accordance with the method for Organic Acid, page 2181.

**Procedure.**—The spectrophotometric measurements shall be made the same day as the extraction is performed.

Extract 6 g. of the sample with two 100-ml. portions of ETA for 1 hour each in accordance with the method for Organic Acid, page 2181, including the final dilution to 250 ml.

Prepare the basic and neutral solutions in two separate 50-ml. volumetric flasks as follows:

*Basic Solution:*

5 ml. ETA extract  
 10 ml. 0.5 N KOH solution  
 Dilute to mark with ethanol

*Neutral Solution:*

5 ml. ETA extract  
 Dilute to mark with ethanol

Prepare the corresponding reference solutions as follows:

*Basic Reference Solution:*

5 ml. ETA solvent  
 10 ml. 0.5 N KOH solution  
 Dilute to mark with ethanol

*Neutral Reference Solution:*

5 ml. ETA solvent  
 Dilute to mark with ethanol

Measure the absorbance of each solution at 301 m $\mu$ , using the corresponding reference solution in the spectrophotometer reference cell in each case. Call the observed absorbance values  $A_{\text{basic}}$  and  $A_{\text{neutral}}$ , respectively.

**Calculation.**—Calculate the percentage of mixed alkylated phenols (MAP) as follows:

$$\text{MAP, per cent} = \frac{A_{\text{basic}} - A_{\text{neutral}}}{(a_{\text{basic}} - a_{\text{neutral}}) \times 2.4} \times 100$$

where the terms are defined in Method C, Reference Standards and Calibration, page 2186, but have the values determined in accordance with the above procedure.

**Reproducibility.**—Results obtained by different analysts in different laboratories on rubber containing 1.0 to 1.8 per cent MAP should be reproducible within  $\pm 0.1$  per cent.

*ETA EXTRACT*

**Scope and Application**—This procedure is intended to determine the various organic constituents in the rubber. It will give the combined amount of rosin and fatty acids soaps oil extenders defoamer tars antioxidants and other uncombined organic constituents. The rubber hydrocarbon can be estimated by subtracting the sum of the ETA (Ethanol Toluene Azeotrope) extract the total ash and the volatile matter from 100.

**Outline of Method**—Thin narrow strips of the dried rubber are extracted three times with 100 ml of hot ETA solvent for 1 hour each and rinsed three times with 10 ml portions of ETA solvent. Although two extractions are sufficient for non-pigmented rubbers three extractions are necessary for oil masterbatch rubbers. The extracted rubber is boiled with 25 ml of acetone decanted and dried. The difference between the original sample and the extracted sample is the ETA extract.

**Apparatus** Wide Mouth Flask 400 to 550 ml

Hot Plate

Filter Paper or a wire gauze or an asbestos mat

**Reagents** Ethanol Toluene Azeotrope (ETA)—See preparation of this reagent in method for Bound Styrene in SBR page 2169

Acetone NF grade

**Preparation of Sample**—Prepare the sample in accordance with the procedure described in test for Organic Acid page 2181

**Procedure**—Accurately weigh a 6 g sample of the dried strips. Add 100 ml of ETA solvent to the 400 to 550 ml flask. Add each strip of the weighed sample separately to the flask swirling the flask after each addition so that each strip is thoroughly wetted with the solvent to avoid sticking. To prevent the sample from sticking to the flask place a filter paper in the bottom of the flask or use a wire gauze or asbestos mat between the flask and the hot plate. Reflux the contents of the flask on the hot plate for 1 hour.

After refluxing decant the ETA extract and discard it. Add a second 100 ml portion of the ETA solvent to the rubber sample and reflux again for 1 hour.

Again decant the ETA extract and discard it. Add a third 100 ml portion of the ETA solvent to the rubber sample and reflux again for 1 hour.

For the third time decant the ETA extract and discard it. Rinse the sample with three successive 10 ml portions of ETA solvent.

Add approximately 25 ml of acetone to the rubber sample remaining in the flask. Heat the acetone to gentle boiling and boil it for approximately 5 minutes.

Decant the acetone and transfer the extracted sample to a tared watch glass. Dry it to constant weight at 105°C and weigh it. (This can be done in 1 hour at 105°C and 29 in. of vacuum in a vacuum oven.)

**Calculation**—Calculate the percentage of ETA extract as follows

$$\text{ETA extract per cent} = \frac{100(A - I)}{A}$$

where  $A$  = weight of the original dry sample and

$I$  = weight of the extracted sample

*OTHER METHODS AND APPLICATIONS*

It should be pointed out that the methods for determination of antioxidants are particularly useful for other crude rubbers and for other antioxidants. It is only

necessary to find a suitable rubber solvent or extractant and a set of conditions satisfactory for the particular combination under consideration. It should also be noted that the standard Soxhlet type of extraction with acetone, azeotropic mixtures or other extracting solvents may be useful for this purpose.

An estimation of the oil content of the oil extended SBR crude (SBR oil masterbatch) may be obtained by running an ETA extract and correcting for other components of the SBR extracted.

The stability of the crude and probably the vulcanized synthetic rubbers toward thermal and oxidative degradation may be affected by the presence of trace metals, particularly copper and iron. The determination of these elements in crude SBR is of importance in some cases, notably for non-staining light colored crude rubbers. The determination of copper and iron may be accomplished by the methods given under analysis of crude natural rubber, pages 2152 and 2155.

# ANALYSIS OF RUBBER COMPOUNDS

## INTRODUCTION

A rubber compound is defined for the purpose of this chapter as a mixture of a natural or synthetic rubber polymer with chemicals and fillers, of such a nature that it is a useful article itself or may be converted to a useful article by suitable treatment. By far the greater number of rubber compounds are vulcanized articles of commerce. However the definition includes such unvulcanized compounds as compounded latex, rubber cements, tire tread compounds used in tire retreading operations, etc. Generally speaking, it is necessary to convert solutions and suspensions to dry solids before applying the analytical methods given in this chapter.

## PREPARATION OF SAMPLES

The following methods of preparing samples of crude rubber, unvulcanized rubber compounds, vulcanized soft and hard rubber compounds are taken from ASTM Designation D297 61T<sup>16</sup>. It should be noted, however, that special modifications of these methods are required in some of the sections concerned with the analysis of crude natural and crude SBR rubbers.

Before preparing a sample for analysis the analyst should, by inspection, assure himself that it has not been contaminated. The sample to be analyzed should be selected by taking pieces from various parts of the original sample and separating them from foreign matter. Because of the variety of rubber products to which this method is to be applied, no single procedure for reducing the sample to the required fineness is applicable to all samples. Therefore, several alternative procedures for this purpose are described in the following paragraphs. The analyst is expected to select the one most suitable to the sample that he is analyzing and the equipment available.

For vulcanized soft rubber, unvulcanized rubber, crude rubber, and many samples of reclaimed rubber, it is preferable to mix the sample and grind it by passing it two or three times through a clean, cold laboratory rubber mill. The rubber will come from the mill in the form of a coarse powder or a rough sheet. If the product is in the form of a sheet, the adjustment of the mill should be such that the thickness of the final sheet is no greater than 0.5 mm. If the sample is sticky, it should be rolled in a liner material that will not adhere to or contaminate the sample. If the milled sample is a powder, it should be transferred to a No. 14 (1410  $\mu$ ) sieve and rubbed through the sieve. Grinding shall be continued until the entire sample passes through the sieve.

In the absence of milling machinery, the sample may be prepared by cutting it with scissors so that it will pass a No. 14 (1410  $\mu$ ) sieve<sup>17</sup>. The sample may be cut into long strips that are fine enough to pass freely through the sieve and the strips

<sup>16</sup> Tentative Methods for Chemical Analysis of Rubber Products, ASTM Designation D297 61T.

<sup>17</sup> Detailed requirements for these sieves are given in the Specifications for Sieves for Testing Purposes (ASTM Designation E11) 1958 Book of ASTM Standards, Part 9.

fed through by hand, or the sample may be cut into small fragments and shaken through the sieve. The cutting shall be continued until the entire sample passes through the sieve. If necessary, to prevent sticking, different fragments of the sieved sample may be segregated by wrapping in a liner material that will not adhere to or contaminate the sample.

Certain very glutinous samples may be prepared for extraction analysis as follows: Place a weighed 2-g. sample of the material between two pieces of ashless filter paper that have been extracted in accordance with the method for Total Extract on page 2205. The papers should be approximately 20 by 4 in. and the sample should be placed near one end. Flatten the sample and spread it throughout the length of the filter paper by passing the "sandwich" lengthwise, through a cold, closely set, even-speed rubber calender. The gross thickness of the resulting sheet should not be greater than 1.0 mm. If a rubber calender is not available, a similar sheet may be obtained by placing the sample in a hydraulic press or a vise. In the latter case, the sample may be roughly spread by hand throughout the length of the filter paper and pressure applied to small areas at a time until the whole sample has been flattened.

Samples of rubberized cloth, whose over-all thickness is no greater than 1.0 mm., may be prepared for analysis by cutting them into pieces 1.5-mm. square and then mixing well. If the fabric is easily removed, it should be separated unless an analysis of the whole cloth is desired.

Samples of rubber cements shall be evaporated to dryness in a vacuum at a temperature not higher than 30°C. The residue may then be analyzed as an unvulcanized sample. A separate sample of the cement shall be distilled under reduced pressure if examination of the solvent is desired.

Samples of hard rubber shall be reduced to powder form by filing, cleaned with a magnet, and sieved through a No. 30 (590- $\mu$ ) sieve.<sup>17</sup> Residue retained on this sieve shall be reduced until the entire sample passes through the sieve.

## IDENTIFICATION OF RUBBER POLYMERS

The identification of the type of rubber polymer present in a vulcanized or unvulcanized rubber compound may be made by the methods given for use with crude rubbers, on pages 2164-2168, provided there is but one rubber present. Occasionally the presence of a second rubber may be detected but the methods should not be used for this purpose except where a trained operator establishes the reliability of the test with known mixtures. It should again be noted that the analysis scheme does not consider all the types of rubber commercially available or any of the newer rubbers with the exception of IR which behaves identically with NR.

A more positive method of identifying polymers, singly or in mixtures, is by the use of infrared absorption spectroscopy. The techniques used for this purpose are essentially standard, differing only in minor details and in the type of equipment used in different laboratories. For compounded, and particularly for vulcanized rubbers, it is rarely possible to press a film as discussed on page 2169, because of interference or scattering by the fillers. However, two techniques are in general use in industrial laboratories. While they undoubtedly differ in detail as used in different laboratories it is felt that a brief description of these methods with some modifications that have proved to be of value would be a useful part of this section.

The first method, essentially that described by Dinsmore and Smith,<sup>18</sup> is a dis-

<sup>18</sup> Dinsmore, H. L. and Smith, D. C., *Anal. Chem.*, 20, 11 (1948).

solution method which may be carried out approximately as follows. Prepare a sample of the rubber compound as directed in method on page 2190, and extract a 1 to 2 g specimen by the total extract method, page 2205 if the specimen is vulcanized, or by the acetone extract method, page 2156, if it is unvulcanized. Dissolve the specimen in 100 to 200 ml of *o*-dichlorobenzene under reflux. This process may be expedited by stirring in such a manner as to prevent the specimen from adhering to the flask and by aerating, particularly during the first part of the dissolution period. Dilute the resulting solution with about 50% of its volume of benzene. If no carbon black is present it may be possible to remove other fillers by centrifugation. In any case, carbon black and other fillers may be removed by adding sufficient Celite filter aid to the solution to make a paste that can just be poured and filtering through a Buchner funnel prepared with filter paper and a layer of Celite wetted with benzene. Concentrate the clear filtrate by vacuum evaporation of solvent until it can be spread on a salt plate. Remove residual solvent by air drying followed by 40 minutes in an 80°C vacuum oven. Run the spectrum on an infrared spectrophotometer from 2.5 to 15 microns. Compare the spectrum with known spectra for identification of polymers, copolymers or mixtures of rubber polymers.

The solution method suffers in some cases by lack of solubility of the rubbers, particularly when present in mixtures. CR rubber and SBR types of high styrene content are difficult to dissolve and may be missed if present in relatively small amounts. Some of the newer elastomers not discussed here are probably not detectable with this technique, particularly those not belonging to the R family of rubbers.

A more rapid and very useful method which may have advantages over the solution method in some cases has been described by Harms,<sup>19</sup> by Kruse and Wallace<sup>20</sup> and by Hummel.<sup>21</sup> The method is based on the examination of the pyrolysis products of the rubbers by infrared absorption spectroscopy. The nature of the pyrolysis products, at least from a qualitative viewpoint, appears to be relatively insensitive to quite large changes in the pyrolysis temperature as long as heating is rapid enough to prevent excessive charring.

In the method described by Harms<sup>19</sup> pyrolysis is carried out in a 15 x 120 mm borosilicate glass test tube using a sample containing about 0.5 g of the rubber polymer. The test tube is placed in an almost horizontal position and the closed end is heated rapidly with a flame to a temperature between 375 and 750°C the temperature depending on the type of rubber. The pyrolysis products that condense on the cool upper portion of the test tube are transferred directly to a salt plate, covered with another salt plate, and the spectrum is run on a spectrophotometer.

In the method described by Kruse and Wallace<sup>20</sup> the test tube containing about 1 g of sample is placed in a cavity in an aluminum block that has been previously heated to 443 to 465°C. In this case a delivery tube in the form of an inverted U is attached to the test tube and the pyrolysis products are collected in carbon tetrachloride. The resulting solution is dried free of water and the infrared absorption spectrum is run.

Hummel<sup>21</sup> prefers to use vacuum pyrolysis and to trap both the liquid and gaseous pyrolysis products. This has an advantage when polymers are present

<sup>19</sup> D. L. Harms, *Anal. Chem.*, **25**, 1140 (1953).

<sup>20</sup> P. F. Kruse, Jr., and W. B. Wallace, *Ibid.*, **1156**.

<sup>21</sup> D. Hummel, *Rubber Chemistry and Technology*, **32**, 854 (1959).

which pyrolyze to low boiling monomers with the production of little or no liquid pyrolyzate.

To use any of the above methods it is necessary to have known spectra for comparison purposes. Standard spectra appear in the above references and also in the book by Wake.<sup>22</sup> These spectra may be adequate for limited use of the methods, but if the methods are to be used extensively it is advisable to build a reference library of spectra run by a given technique and to include mixtures of polymers in different proportions. There is a possibility of interference from rubber additives in all of the above methods. Extraction is therefore advisable except in the case of crude rubbers known to contain no added oils.

## DETERMINATION OF RUBBER POLYMER CONTENT

*Introduction.*—There are two standard general methods of determining the rubber polymer content of a rubber compound. Unfortunately, they are not both applicable to all compounds and in some cases neither method results in a completely satisfactory answer. Method A is the Direct Method, applicable only where an unambiguous method exists for the direct determination of a rubber polymer or a mixture of rubber polymers. In terms of existing well-proven methods, only three types of rubbers may be determined directly; NR and IR, CR and NBR, the latter only when the acrylonitrile (or nitrogen) content of the crude NBR used in the compound is known. Obviously the list of applications must include any new or existing specialty rubbers whose nitrogen or chlorine contents are known if these elements can be satisfactorily determined by the methods included here. Method B, the Indirect Method, is more generally applicable but has the disadvantage of any indirect method; the errors are cumulative and result in considerable error in the rubber polymer determination.

### METHOD A—DIRECT METHOD

#### NATURAL OR SYNTHETIC ISOPRENE POLYMERS

The polyisoprene content of NR or IR rubber in a compound may be determined in accordance with the method described in the section on Isoprene Polymer, page 2161.

#### CHLORINE-CONTAINING POLYMERS

CR rubber content, whether present as polychloroprene, as a copolymer with chloroprene, or as some other chlorine-containing "R" family rubber, may be determined by the method given in the section on the Chlorine Content of CR Rubbers, page 2174, if the chlorine content of the rubber polymer used in the compound is known. The presence of more than one chlorine-containing rubber would be a rare occurrence. Pure CR rubber is nominally assumed to have 37% chlorine in the commercial product.

#### NITROGEN-CONTAINING POLYMERS

In this case the nature of the nitrogen-containing polymer or copolymer must be well known if unambiguous results are to be obtained. Nitrogen in a rubber

<sup>22</sup> W. C. Wake, "The Analysis of Rubber and Rubber-Like Polymers," MacLaren and Sons, Ltd., London, 1958.



compound may be determined by the method given in the section on the Nitrogen Content of NBR Rubbers, page 2172, but the determination of the quantity of a nitrogen containing polymer present in the compound requires a knowledge of the acrylonitrile content of the NBR rubber, the pyridine content of the PBR rubber or the composition of the polyurethane (U family) rubber that was used in the rubber compound. Interference due to the presence of nitrogen bearing antioxidants and accelerators may be essentially eliminated by extraction with a suitable solvent. Ketones are not usually satisfactory because of solubility of the rubbers frequently even in the vulcanized state. Ethanol-toluene azeotrope may be used in most cases.

### STYRENE-CONTAINING POLYMERS

Bound styrene (polystyrene as homo- or copolymer) in a rubber compound containing SBR or other styrene containing rubbers or resins may be determined chemically with a fair degree of accuracy by a method originally proposed by Hilton Newell and Tolsma.<sup>23</sup> This method in a modified form is given below as it appears in ASTM Designation D297 61T<sup>26</sup>. It is most reliable on crude SBR and on SBR compounds containing no other rubbers but will give good results on rubber products containing other rubbers if proper corrections are made by means of standard control samples.

**Scope**—This method is intended for the determination of the bound styrene content of SBR polymers or rubber products containing SBR polymers including those products containing carbon black, oil extended SBR polymers, inorganic fillers, NR, IR, and CR. Application to rubber products containing other polymers shall be verified by the use of control samples of known and similar composition. The method is considered to provide an estimation of SBR content because the bound styrene content of the entire sample is determined. SBR content can be estimated by assuming the bound styrene content of the SBR used in the rubber product.

The method is designed for routine application in cases where the accuracy desired does not warrant the calibration of the spectrophotometer. There is also provision for increasing the accuracy of results by calibration of the spectrophotometer.

**Summary of Method**—The bound styrene is nitrated and oxidized to nitrobenzoic acid which is separated by extraction and is determined quantitatively by measuring its ultraviolet absorption at 265, 273.75, and 285  $m\mu$ . A preliminary alcohol extraction removes interfering compounds.

**Apparatus.** Spectrophotometer.—A photoelectric spectrophotometer that will measure absorbance in the region from 260 to 290  $m\mu$ .

Absorption Cells, silica, 1 cm. path length.

Extraction Apparatus—Soxhlet extraction apparatus or ASTM extraction apparatus (see Acetone Extract, page 2156).

Boiling Flasks, 125 ml., with standard taper joints.

Graham Condensers, with water cooled outer and inner joints.

Boiling Chips, carborundum, No. 10 grit.

**Reagents**—Diethyl Ether, peroxide free.

Ethyl Alcohol, denatured, Formula 3A, or undenatured ethanol (95%).

Nitric Acid (sp. gr. 1.42)—Concentrated nitric acid ( $\text{HNO}_3$ ).

<sup>23</sup> C. L. Hilton, J. E. Newell and J. Tolsma, *Anal. Chem.* **31**, 915 (1959).

**Sodium Chloride Solution (Saturated).**—Prepare a saturated solution of sodium chloride (NaCl) in water.

**Sodium Hydroxide Solution (200 g. per l.).**—Dissolve 200 g. of sodium hydroxide (NaOH) in water and dilute to 1 liter.

**Sodium Hydroxide Solution (4 g. per l.).**—Dissolve 4 g. of NaOH in water and dilute to 1 liter.

**Sodium Sulfate, Anhydrous ( $\text{Na}_2\text{SO}_4$ ).**

**Preparation of Sample.**—Mill mass polymer or rubber product sample and sheet out to less than 0.5 mm. thickness.

**Calibration of Spectrophotometer.**—While calibration of the spectrophotometer used in the procedure is not always necessary, for the most accurate results, a calibration is desirable, using standard samples of styrene-containing copolymers having bound styrene contents approximately the same as the copolymer present in the unknown rubber product sample. A calibration with a production sample of SBR, preferably in the 23.5% bound styrene range, will be suitable for reasonably accurate measurements on rubber products containing SBR with from 9 to 45 per cent bound styrene. In the presence of other rubbers, calibration to give maximum accuracy will probably require the use of a known SBR together with a known amount of any other rubber present in order to obtain a correction for absorptivity of nitrated products of the other rubber.

Determine the bound styrene content of a reference standard SBR by treating a sample of crude SBR polymer having the appropriate bound styrene content in accordance with the refractive index method covered in the section on Bound Styrene in SBR, page 2169. Determine the bound styrene content of the reference standard in triplicate, or with more replications if a greater confidence must be placed in the mean value obtained.

**NOTE.**—For most accurate calibration, use a sample of hot SBR, preferably of type 1006 of the Recommended Practice for Description of Types of Styrene-Butadiene Rubbers (SBR) and Butadiene Rubbers (BR) (ASTM Designation: D1419), for 23.5 per cent bound styrene. Other 1000 series samples may be used, but they should be fatty acid emulsifier, salt-acid coagulated polymers.

Treat replicate specimens (at least triplicate) of the samples that have been dried and pressed between sheets of foil in the refractive index method for determination of bound styrene content, in accordance with the nitration procedure given on p. 2196. Calculate the average absorptivity due to nitrated styrene at each wavelength as follows:

$$a_s = \frac{\frac{A_p}{c} - a_b(1 - X)}{X}$$

where  $a_s$  = absorptivity due to nitrated styrene,

$A_p$  = absorbance of the solution,

$c$  = concentration of specimen in solution on which absorbance is measured, in g. per l.,

$X$  = average value of the fraction of bound styrene in copolymer, and

$a_b$  = absorptivity of nitrated butadiene = 0.373 at 265  $m\mu$ , 0.310 at 273.75  $m\mu$ , and 0.265 at 285  $m\mu$ .

**NOTE.**—The nomenclature and abbreviations used in this method are in accordance with the Definitions of Terms and Symbols Relating to Absorption Spectroscopy (ASTM Designation: E131), 1961 Book of ASTM Standards, Part 7.

Record the slit widths used in determining the above absorbance values and use approximately the same slit widths in the analysis of unknown samples. An improvement in precision may result if the final solution used in calibration and in the determination is approximately half of the concentration specified in the procedure. Absorbance values will then be in the 0.4 to 0.7 range.

**Procedure**—Accurately weigh a specimen of the desired size (NOTE) and extract it with ethanol for 16 to 18 hours in a Soxhlet extraction apparatus or in the ASTM extraction apparatus described in the section on Acetone Extract p 2156. Dry the extracted specimen in a vacuum oven at 100°C for 1 hour.

**NOTE**—Estimate the specimen weight by means of the following formula

$$\text{Specimen weight g} = \frac{45}{\text{estimated per cent styrene in sample}}$$

Transfer the extracted and dried specimen to a 125 ml flask having a standard taper joint and add 20 ml of  $\text{HNO}_3$  and a few carborundum boiling chips. Place the flask on a cold hot plate, turn the heat on and allow to reflux at a rolling boil overnight (16 to 18 hours) under a water cooled Graham condenser. Turn off heat, pour 10 to 20 ml of water into the top of the condenser and allow the water to be drawn into the flask as the flask cools. Allow the reaction mixture to cool to permit handling of the flask.

Transfer to a 400 ml beaker using a stream of water from a wash bottle to rinse the flask and the standard taper joints. Add the rinsings to the beaker. Cool the beaker to room temperature. Add 50 ml of NaOH solution (200 g per liter) to the original flask and again rinse into the beaker using water. Test the solution in the beaker with pH paper. The solution should be made strongly acid with  $\text{HNO}_3$  if the solution is not already strongly acid at this point. Cool to room temperature. Transfer the solution to a 500 ml separatory funnel, rinse the beaker with water and add the washings to the separatory funnel. (Caution—The skill with which these transfers and the subsequent extractions are performed will determine the accuracy of the analysis.)

Shake the solution with 50 ml of diethyl ether and allow the layers to separate. Drain the lower aqueous layer into the original beaker. Add 25 ml of the saturated salt solution to the ether layer. Drain a few milliliters into the original beaker to wash the stem of the separatory funnel. Shake and allow layers to separate. Drain the salt solution into the same beaker. Drain the ether layer into a 250 ml beaker containing 4 to 5 g of anhydrous  $\text{Na}_2\text{SO}_4$ . Add 50 ml of ether to the separatory funnel and drain a few milliliters into the 250 ml beaker containing the ether extract to wash the stem of the funnel. Swirl ether in the beaker and transfer ether to another separatory funnel.

Repeat extraction of the aqueous layer in the same manner for a total of three extractions, each ether extract being dried over the same  $\text{Na}_2\text{SO}_4$  and collected in the second separatory funnel.

Extract the combined ether extracts four times with 50 ml portions of NaOH solution (4 g per liter). Collect the aqueous extracts in a 250 ml volumetric flask. After each extraction, drain a few milliliters of the next portion of NaOH solution before shaking to rinse the stem of the separatory funnel, adding the drainings to the volumetric flask. Dilute to volume with NaOH solution (4 g per liter). Mix well. Pipet a 25 ml aliquot into a second 250 ml volumetric flask. Dilute to volume with NaOH solution (4 g per liter) and mix well.

With NaOH solution (4 g. per l.) in the blank cell and the extract in a matched silica absorption cell, measure the absorbance at 265  $m\mu$ , 273.75  $m\mu$ , and 285  $m\mu$  using a spectrophotometer. The dark current should be adjusted before and after each reading. If the dark current is found to have drifted during the reading, the reading should be repeated.

Calculations.—(1) If the spectrophotometer has not been calibrated, calculate the apparent percentage bound styrene as follows:

$$S_1 = \frac{A_{265} \times 3.829}{B} - 0.57Y$$

$$S_2 = \frac{A_{273.75} \times 3.611}{B} - 0.45Y$$

$$S_3 = \frac{A_{285} \times 4.018}{B} - 0.43Y$$

$$\text{Bound styrene, per cent} = \frac{S_1 + S_2 + S_3}{3}$$

where  $A$  = absorbance at the specified wavelength,

$B$  = weight of specimen, in g., and

$Y$  = fraction of styrene-containing copolymer in sample. (See NOTE below.)

(2) If the spectrophotometer has been calibrated as directed in this method, calculate the percentage of bound styrene content as follows (see NOTE below):

NOTE.—The use of absorbance at three wavelengths serves to correct for background due to minor interferences. An unknown sample of crude SBR having a bound styrene content close to that of the SBR used for calibration should give  $S_1$ ,  $S_2$ , and  $S_3$  values as calculated by (2) above that do not differ by more than a few tenths of a per cent. Other types of samples may yield values of  $S_1$ ,  $S_2$ , and  $S_3$  having a range as great as 1% before the analysis is suspected of error due to interference. With the use of the formula given in (1) above, however, the range of  $S_1$ ,  $S_2$ , and  $S_3$  values may be as great as 2%, because of improper wavelength calibration of the spectrophotometer and because the constants in the formula may not be correct for the particular spectrophotometer. Any results in which this range is greater than 2% should be considered suspect from the standpoint of interferences.

$$\text{Bound styrene, per cent} = \frac{S_1 + S_2 + S_3}{3}$$

$$S_1 = \frac{\frac{100 A_{x(265)}}{c_x} - 37.3Y}{a_s(265) - 0.373}$$

$$S_2 = \frac{\frac{100 A_{x(273.75)}}{c_x} - 31.0Y}{a_s(273.75) - 0.310}$$

$$S_3 = \frac{\frac{100 A_{x(285)}}{c_x} - 26.5Y}{a_s(285) - 0.265}$$

where  $c_x$  = concentration of specimen solution on which absorbance is measured, in g per l,

$A_x$  = absorbance of solution at specified wavelength,

$a_x$  = absorptivity at specified wavelength as determined and

$Y$  = fraction of styrene-containing copolymer in sample (Note)

**NOTE**—The fraction of styrene containing copolymers in the sample may not always be known but can usually be estimated with sufficient accuracy. For samples where the fraction of styrene containing copolymers is not known but where the percentage of bound styrene in the copolymer in the sample is approximately known, an equally accurate final value for percentage of bound styrene may be obtained as follows. Calculate  $S_1$ ,  $S_2$  and  $S_3$  with the assumption that  $Y = 1$ . Calculate values for  $Y$  based on these apparent bound styrene percentages and recalculate  $S_1$ ,  $S_2$  and  $S_3$ .

### IIR OR POLYISOBUTYLENE DETERMINATION

A rubber product containing no polymer other than IIR can be analyzed for IIR content by inert atmosphere pyrolysis of an extracted sample as described by Wake.<sup>20</sup> Another method, developed by Kress<sup>21</sup> and adopted with revisions by ASTM<sup>16</sup> is more generally useful for any type of compound containing IIR or polyisobutylene. It is particularly useful for analyzing for low quantities of IIR present as in unintentional contamination in rubber products. There appears to be a negative error that may best be corrected for in routine analysis by the use of controls. This error is probably of no consequence in testing for the presence of contamination.

**Scope**—This method is intended for use in the determination of IIR or polyisobutylene in rubber products. The method is especially useful in the determination of small amounts of IIR in rubber products. It is applicable to products containing BR, CR, IR, NR, NBR, and SBR rubbers. Application to products containing other polymers must be verified by use of control samples of known and similar composition.

**Summary of Method**—Rubbers having unsaturated carbon chains are destroyed by digestion with nitric acid. The polymers IIR and polyisobutylene are not attacked. The residue after filtration is heated with *t*-butyl hydroperoxide solution to solubilize the IIR. After filtration to remove any remaining fillers the IIR or polyisobutylene is precipitated with alcohol, dried, and weighed.

**Apparatus and Materials**—Steam Plate or Hot Plate maintained at 140°C in a fume hood, and a thermometer to measure surface temperature.

Reflux Condensers, Hopkins type, with standard taper 24/40 joints.

Erlenmeyer Flask, 250 ml, with standard taper joints.

Bumping Stones, No. 6 Carborundum.

Buchner Funnel A—A No. 0 Buchner funnel lined first with a Reeve Angel No. 934 AH glass-fiber disk, then with medium fiber asbestos to about  $\frac{1}{8}$  in. depth and finally with a  $\frac{1}{8}$  in. top layer of diatomaceous earth filter aid from a suspension in acetone to a total depth of about  $\frac{1}{4}$  in. Remove the acetone with suction and age at least 24 hours before using.

**NOTE**—The preparation of the filter funnels as described has been found to be important to the success of the method. The use of other materials of equivalent properties in the preparation of the filters should be tested with samples of known composition.

<sup>21</sup> K. E. Kress, *Anal. Chem.*, **30**, 287 (1958).

**Büchner Funnel B.**—A No. 1 Büchner funnel lined first with a circle of S & S No. 598 filter paper, then with medium-fiber asbestos to a depth of about  $\frac{1}{8}$  in. and finally with a  $\frac{1}{8}$ -in. top layer of diatomaceous earth filter-aid from a suspension in acetone to a total depth of about  $\frac{1}{4}$  in. Remove the acetone with suction. Wash with the equal volume mixture of chloroform and 30 to 60°C. petroleum ether. Remove the solvent mixture with suction. Age at least 24 hours before using. (See NOTE above.)

**Diatomaceous Earth Filter Aid.**

**Asbestos Filtering Fiber, medium.**

**Reagents.** Acetone.

**Chloroform.**

**Chloroform-Petroleum Ether Mixture (1:1).**—Mix equal volumes of chloroform and petroleum ether.

**Ethanol.**—Formula 2B denatured ethyl alcohol or absolute ethanol.

**Petroleum Ether,** 30 to 60°C. boiling range.

**Tert-Butyl Hydroperoxide,** commercial grade.

**Xylene.**

**Procedure.**—Homogenize and sheet out the sample with a tight rubber mill to a thickness of 0.5 mm. Accurately weigh a specimen of appropriate size to contain between 0.05 and 0.20 g. of polyisobutylene. Do not use more than 5 g. Use 1 g. for unknown range and repeat with adjusted sample size if less than 0.05 g. or more than 0.20 g. is found. Add to 200 ml. of acetone in a 250-ml. Erlenmeyer flask, connect to a reflux condenser, and reflux 1 hour. Remove the sample, blot off acetone with a paper towel, and dry for 10 minutes in an oven at 105 to 110°C.

Cut into 5- by 10-mm. or smaller pieces and place in a 250-ml. beaker. Add 10 ml. of  $\text{HNO}_3$  and allow to stand at room temperature in a hood until initial frothing reaction subsides. If the reaction is slow, warm the beaker on a hot plate at 140°C. until fuming just begins and then remove immediately. If there is no reaction after 5 minutes on a hot plate at 140°C., remove anyway. When all reaction stops and the beaker has cooled to room temperature, add 50 ml. of  $\text{HNO}_3$  and 10 ml. of xylene. Place on a hot plate at 140°C., cover with a watch glass, and digest 30 minutes. Remove the watch glass and digest at least 30 minutes more until xylene is completely evaporated.

Add 1 level teaspoon of filter aid, stir with a glass rod, and filter hot through an aged prepared Büchner funnel A into a 500-ml. filtering flask containing 100 ml. of water. Use low to moderate suction and a fume hood. Wash beaker and filter twice with 20-ml. portions of  $\text{HNO}_3$  at room temperature. Wash copiously with at least 300 ml. of hot water until the filtrate is colorless. Discard the filtrate and rinse the flask with water. Attach the filter to the cleaned filter flask, wash with 50 ml. of ethanol, and dry on the filter with continued suction.

**Caution.**—There is danger of a violent reaction between nitric acid and alcohol.

With the aid of a spoon or spatula, carefully transfer the contents of the funnel to a dry 250-ml. Erlenmeyer flask. Use filter paper wet with chloroform to clean the last traces from the funnel. Add six to ten carborundum bumping stones, 100 ml. of chloroform, 100 ml. of petroleum ether, and 5 to 7 ml. of *tert*-butyl hydroperoxide. Connect to Hopkins condenser and reflux rapidly at least 4 hours. Replace any appreciable amount of evaporated solvent with chloroform-petroleum ether mixture (1:1).

Filter the refluxed sample warm through an aged prepared Buchner funnel B into a clean, dry 500 ml filtering flask, using moderate suction (Too much suction may cause some carbon black to pass through the filter and necessitate refiltering). With a wash bottle, wash the flask and filter five times with 20 ml portions of warm chloroform petroleum ether mixture (1:1). Be sure to wash well the edge and side wall of the funnel with the stream from the wash bottle.

Add two No. 6 carborundum bumping stones to a clean 250 ml beaker. Evaporate portions of the above filtrate in the 250 ml beaker until all the filtrate has been reduced to a small volume. Wash the filter flask well with the chloroform petroleum ether mixture (1:1). Add these washings to the beaker and evaporate to about 20 ml. Transfer the solution to an accurately weighed, clean, dry 50-ml Erlenmeyer flask containing two No. 6 carborundum bumping stones and wash the beaker well with the chloroform petroleum ether mixture (1:1). Carefully evaporate to about 1 to 3 ml on a hot plate at 140°C. Do not evaporate to dryness. Allow the flask to cool to room temperature and then add 25 ml ethanol. (If there is no precipitate or turbidity at this point polyisobutylene is not present and analysis may be terminated.) Boil gently on a hot plate at 140°C for at least 15 minutes, until the alcohol is clear and all the isobutylene coagulates and adheres to the flask. If turbidity persists, evaporate to about 2 to 3 ml, cool to room temperature, and add 25 ml of acetone.

Cool to room temperature and carefully decant the alcohol (or acetone). Wash the precipitated polyisobutylene by swirling gently with 25 ml of acetone at room temperature and decanting. Dry the flask and polyisobutylene 2 hours in an oven at 105 to 110°C, cool in a desiccator, and weigh.

Calculations.—Calculate the percentages of polyisobutylene and IIR as follows

$$A = \frac{B - C}{D} \times 100$$

$$\text{IIR, per cent} = A \times 1.03$$

where  $A$  = percentage of polyisobutylene,

$B$  = weight of flask and precipitated polyisobutylene,

$C$  = weight of flask, and

$D$  = weight of sample used

### INFRARED METHODS

The infrared methods, while lacking in the high accuracy expected of an analytical method, may become the most practical means of estimating, and in some cases determining, the amount of some polymers or polymer mixtures in a rubber compound. Since each case requires a study of the spectra involved and the determination of the absorption bands and band intensity ratios to use for analysis as well as a careful calibration with known compounds, it is beyond the scope of this book to present a standard method. Quantitative methods have been reported by Tryon, Horowitz and Mandel<sup>25</sup> for the determination of NR in mixtures with SBR and by Dinsmore and Smith<sup>26</sup> for determination of NR/SBR mixtures and for determination of the bound polyacrylonitrile content of NBR. These papers provide techniques and a basis for other quantitative methods.

<sup>25</sup> M. Tryon, L. Horowitz and J. Mandel, *J. Res. Natl. Bur. Stds.*, **55**, 219 (1953).

## INDIRECT METHOD

**Introduction.**—This is the standard method that has been used for years by the ASTM,<sup>25</sup> the British Standard Institution<sup>26</sup> and the United States Federal Government.<sup>27</sup> It is based on determination of rubber content by difference when all other compounding ingredients have been determined. It is quite reliable when a simple rubber compound is involved containing only acetone and chloroform extractables, carbon black, sulfur, zinc oxide and other inorganic fillers that will not decompose or change on ashing or that may be determined directly. Fortunately, in high quality rubber compounds today there is not found a large variety of inorganic fillers. In particular, antimony sulfide, lead oxide, barium carbonate and lithopone are not commonly used ingredients. However, it is not uncommon to find clay, hydrated silica, asbestos, talc or calcium carbonate in a rubber compound. When these materials which decompose at ashing temperature (550°C.) are present there is no accurate method of determining the inorganic filler content unless corrections can be applied for loss of water of hydration, carbon dioxide, etc. The exact analysis of fillers, and hence the accurate indirect calculation of rubber content, is therefore not always possible. However, since lead, antimony, calcium, barium as the carbonate or the sulfate, magnesium, zinc and titanium can be determined by methods given in this chapter, and since the approximate amount of hydrated fillers can be determined from the determination of silica, insolubles, and  $R_2O_3$ , it is possible to reconstruct an inorganic filler analysis by determination of ash and some of the individual components with a reasonable degree of accuracy in most cases. The greatest uncertainty is the degree of hydration of the fillers.

The following is basically an abstract of the current ASTM method<sup>16</sup> of calculating rubber by difference. It should be noted that two common synthetic rubbers, CR and NBR, have been omitted from consideration. These polymers, even when vulcanized, may be partially soluble in the extracting solvents, and the use of the method for their determination should be limited to cases where samples of known and similar composition can be successfully analyzed. The same argument holds for the less common specialty rubbers for which no standard methods have yet been proposed.

*RUBBER POLYMER CONTENT BY THE INDIRECT METHOD*<sup>16</sup>

**Scope.**—The rubber content of a product is calculated by subtracting the sum of the nonrubber constituents from 100 per cent. The method is applicable to NR, IR, SBR, and BR products. It can also be applied to IIR products if they are extracted with methyl ethyl ketone rather than with acetone.

**Definitions.** Rubber Polymer is the characteristic and major component of a natural or synthetic crude rubber.

Rubber as Compounded is approximately equivalent to the nonextended rubber used in the manufacture of a rubber product. It differs from the rubber polymer by the amount of nonrubber material present in the crude rubber. For synthetic rubbers the quantity varies with the type of rubber and the manufacturer and no definite percentage can be given. Therefore, for synthetic rubber, rubber as com-

<sup>26</sup> British Standard Methods of Testing Vulcanized Rubber, B.S. 903, British Standard Institution, London, 1950.

<sup>27</sup> Federal Test Method Standard No. 601, Rubber: Sampling and Testing, General Services Administration, Washington, D. C.



pounded shall be considered to be equal to rubber polymer except for SBR (see Table 43 6)

TABLE 43 6 FACTORS FOR CALCULATIONS

Rubber	<i>A</i>	<i>D</i>	Specific Gravity
NR	94/97	0 94	0 91 *
IR	1 00	1 00	0 95 *
SBR *	1 00	0 92	0 94 *
BR	1 00	1 00	0 90 *
IIR	1 00	1 00	0 92 *

\* Containing 23 5 per cent bound styrene and no<sup>†</sup> oil-extended

<sup>†</sup> L. A. Wood Values of Physical Constants of Rubber, Rubber Chemistry and Technology 12, 130 (1939)

\* W. C. Wake, The Analysis of Rubber and Rubber-Like Polymers, MacLaren and Sons Ltd, London, England (1958) pp 42 to 45

Rubber Polymer by Volume is the percentage by volume of a rubber product occupied by the rubber polymer

Rubber by Volume is the percentage by volume of a rubber product occupied by the rubber as compounded

Calculations—Calculate the percentages of rubber as follows

$$\text{Rubber polymer, per cent} = A(100 - B)$$

$$\text{Rubber as compounded, per cent} = \frac{C}{D}$$

$$\text{Rubber polymer by volume, per cent} = \frac{CE}{F}$$

$$\text{Rubber by volume, per cent} = \frac{GE}{F}$$

where *A* = factor listed in Table 43-6,

*B* = sum of percentages of total extract, alcoholic potash extract, organic sulfur, inorganic fillers, free carbon and glue,

*C* = rubber polymer, per cent,

*D* = factor listed in Table 43 6,

*E* = specific gravity of product,

*F* = specific gravity of rubber listed in Table 43-6, and

*G* = rubber as compounded, per cent

## DETERMINATION OF NONRUBBER COMPONENTS

### INTRODUCTION

As can be readily seen from the description of the Indirect Method of Rubber Polymer Determination, several types of analysis are required to determine the

nature and the amount of the non-rubber constituents of a rubber product before calculation of rubber polymer content can be made. In addition, it is frequently of interest to know more than the essential facts necessary to calculate rubber polymer content. It is useful to have information on the types of sulfur present, the types and amounts of organic and inorganic fillers used and the accelerators and age resisters used in the compound. The remaining sections in this chapter are devoted to details of the methods of analysis of extracts, sulfur types, fillers and the identification of accelerators and age resisters. All of the methods except those concerning the last item are taken from ASTM Designation D297-61T<sup>16</sup> except where otherwise noted.

### QUALITATIVE NONRUBBER CONSTITUENTS

There are several qualitative tests for nonrubber constituents that should be performed prior to analysis of a rubber sample of unknown composition. These tests are intended for use in determining the number and kind of analyses that should be conducted on the rubber product.

**Carbonates.**—Drop a small piece of sample into a test tube containing HCl saturated with bromine. If a stream of bubbles is given off, carbonates are present. The test is not applicable to IIR products.

**Antimony and Lead.**—Ash a 0.2 to 0.3-g. specimen. Dissolve the ash in 10 ml. of HCl by heating. Dilute to about 40 ml. and decant or filter the solution from the residue. Pass  $H_2S$  into the solution. If a red-orange precipitate forms, antimony is present and may be determined on a rubber specimen in accordance with the method on page 2220. Organic sulfur shall be determined in accordance with the section on fusion method, page 2211. Dilute with water to about 400 ml. and again pass in  $H_2S$ . If a black precipitate appears, lead is present and organic and inorganic sulfur shall be determined in accordance with the sections on fusion method and inorganic sulfur, antimony absent, pages 2211 and 2212.

**Carbon Black.**—Heat a portion of the sample with  $HNO_3$  until there is no more frothing. If the liquid is black, it indicates the presence of free carbon. The test is not applicable to IIR products.

**Barium Salts.**—If the sample contains carbonate, ash a small specimen, digest the ash in dilute HCl, cool, and filter. Add a few drops of dilute  $H_2SO_4$  to the filtrate. A white precipitate insoluble in excess HCl indicates the presence of acid-soluble barium salts. The presence of acid-soluble barium salts requires that organic sulfur shall be determined by the fusion method on page 2211.

**Waxy Hydrocarbons.**—If waxy hydrocarbons are present, they will solidify at  $-5^\circ C.$  in the acetone extract as a white flocculent precipitate clinging to the sides of the flask.

**Glue.**—Extract a portion of the sample with a mixture of 32 per cent acetone and 68 per cent chloroform by volume for 8 hr. Dry the specimen and digest for 1 hr. with hot water. Filter, cool, and add a few drops of a freshly prepared solution of tannic acid (20 g. per liter) to the filtrate and allow to stand for a few minutes. If the solution becomes turbid, glue is present and should be determined as described on page 2223.

**Factice.**—Digest the rubber remaining from the test for glue with NaOH solution (175 g. per liter). Decant the liquid, dilute, and acidify with HCl. Any cloudiness or precipitate indicates the presence of factice and the alcoholic potash extract should be determined by the method on page 2206.

**Other Fillers**—An HCl soluble ash indicates the absence of clay silica silicates titanium dioxide barium sulfate and lithopone. An HCl insoluble ash indicates the need for a complete ash analysis if composition of the ash is required.

### EXTRACT ANALYSIS

**Scope**—The extract analysis is intended for the removal of materials soluble in the solvents used for the purpose of analysis of the soluble materials themselves and for the prevention of certain materials from interfering in subsequent tests made on the rubber or compound. The tests are applicable to natural rubber compounds and to SBR copolymers. General application of these tests to other synthetic rubbers must be made with caution as there is little data as to the accuracy of the methods for other materials. NBR rubbers for example cannot be analyzed by this group of tests because of swelling and partial solubility of the rubbers. The descriptions of terms are based on current ASTM practice and the Extract Analysis procedures are those found in ASTM Designation D297 61T<sup>14</sup> with appropriate editorial changes suitable for this chapter.

**Description of Terms**—There are four extracting procedures used with various tests carried out on them.

**Acetone Extract**—The acetone extract of vulcanized rubber is generally the total material extracted with acetone. This extract usually contains rubber resins free sulfur mineral oils or waxes (if present in the sample) acetone soluble antioxidants and organic accelerators or their decomposition products and a portion of any bituminous substances or vulcanized oils that may have been used.

Acetone extract corrected is the value obtained by determining the percentages of free sulfur waxy hydrocarbons and mineral oil and subtracting these percentages from the acetone extract figure.

Organic acetone extract is the acetone extract minus the percentage of free sulfur only.

The acetone extract is determined according to the method starting on page 2206.

**Chloroform Extract**—The chloroform extract is determined after the rubber compound has been extracted with acetone. This procedure removes a portion of the bituminous substances and serves as an indication of their presence. The chloroform extract may also include other materials as well as small amounts of rubber for which no correction is made. This extraction procedure should not be used for crude unvulcanized or reclaimed rubbers and should be applied to synthetic rubbers other than SBR types only when experience indicates that the results are useful. The chloroform extract is determined according to the method starting on page 2205.

**Total Extract**—The total extract is the material removed by extraction with a mixture of acetone and chloroform and is approximately equal to the sum of the acetone and chloroform extracts. The same precautions as apply to the acetone and the chloroform extracts separately also apply to the mixed solvents. The total extract is determined according to the method starting on page 2205.

**Alcoholic Potash Extract**—This method is intended to detect the presence of and aid in determining the amount of rubber substitutes in natural and SBR rubbers. The method is applied to compounds previously extracted with acetone and chloroform as described or after total extract has been determined. The method may not be of value for rubbers other than NR and SBR types.

The alcoholic potash extract is determined according to the method starting on page 2206.

The following three tests are carried out on the acetone extracts.

**Unsaponifiable Actone Extract.**—This determination is carried out on the acetone extract obtained according to the method presented on page 2207, and is intended to determine the amount of unsaponifiable materials such as waxy hydrocarbons or mineral oil in the acetone extract. The unsaponifiables are defined as that portion of the acetone extract not saponified by a 1 *N* alcoholic KOH solution.

**Waxy Hydrocarbons.**—These are defined as the materials extractable with absolute ethanol from the unsaponifiable acetone extract obtained according to the method on page 2207. These waxy hydrocarbons are the materials separating from the absolute alcoholic solution on cooling to  $-5^{\circ}\text{C}$ .

The determination is made according to method on page 2207.

**Mineral Oil.**—Mineral oil is defined as the part of the unsaponifiable acetone extract that is soluble in absolute ethanol at  $-5^{\circ}\text{C}$ ., and is soluble in  $\text{CCl}_4$  and is not attacked by concentrated  $\text{H}_2\text{SO}_4$ . It is determined on the supernatant ethanol layer from the waxy hydrocarbon determination described in method on page 2207. The procedure for the mineral oil determination is described in method on page 2207.

### ACETONE EXTRACT

This procedure is carried out in the same way for rubber compounds as for crude rubber as described on page 2156, using a specimen prepared as described on page 2190.

### CHLOROFORM EXTRACT

**Apparatus.**—The extraction apparatus should be that described for Acetone Extract. (See page 2156.)

**Procedure.**—Suspend the extraction cup containing the rubber specimen that has been extracted with acetone in a second weighed extraction flask containing 50 to 75 ml. of chloroform and extract it for 4 hours with the chloroform. (Hard rubber and any soft rubber sample having a ratio of total sulfur to rubber polymer in excess of 10% shall be extracted for 24 hours.) Record the color of the chloroform solution. Evaporate the chloroform over a steam bath, using a gentle current of filtered air to prevent boiling. Remove the flask from the steam bath just prior to the disappearance of the last traces of solvent to prevent loss of extract. Continue the passage of air for 10 minutes to remove the remaining solvent and dry the flask for 2 hours in an air bath at  $70 \pm 5^{\circ}\text{C}$ . Cool in a desiccator to the temperature of the balance and weigh. Reserve the extracted sample for extraction with alcoholic potash.

**Calculation.**—Calculate the percentage of chloroform extract as follows:

$$\text{Chloroform extract, per cent} = \frac{\text{wt. of extract}}{\text{wt. of specimen}} \times 100$$

### TOTAL EXTRACT

**Apparatus.**—The extraction apparatus shall be that described for Acetone Extract. (See page 2156.)

**Procedure.**—Place a weighed specimen of approximately 2 g. in a filter paper. If the specimen is in the form of a sheet, cut it with scissors into strips 3 to 5 mm. in width. If the specimen may become tacky during the extraction, take care that adjacent portions are separated by paper. Fold the paper so that it will fit in the

extraction cup and suspend the cup in a weighed extraction flask containing 30 to 70 ml of a mixture consisting of 32 parts of acetone and 68 parts of chloroform by volume (Prior to the weighing of the extraction flask it shall have been dried for 2 hr at  $70 \pm 5^\circ\text{C}$  and cooled in a desiccator to the temperature of the balance.) Extract the specimen continuously for 16 hours heating at a rate such that the time required to fill and empty the siphon cup will be between 20 and 30 minutes. (Hard rubber and any soft rubber specimen having a ratio of total sulfur to rubber hydrocarbon in excess of 10% shall be extracted for 72 hours.) Carefully note all characteristics of the extract both when hot and cold. If the color is black make a chloroform extraction and add the value for chloroform extract to the result obtained for total extract. Evaporate off the solvent over a steam bath using a gentle current of filtered air to prevent boiling. Remove the flask from the steam bath just prior to the disappearance of the last traces of solvent to prevent loss of extract. Continue the passage of air through the flask for 10 minutes to remove the remaining solvent and dry the flask for 2 hours in a  $70 \pm 5^\circ\text{C}$  air bath. Cool in a desiccator to the temperature of the balance and weigh. Save the extracted rubber for further tests that require the use of an extracted specimen.

**Calculation**—Calculate the percentage of total extract as follows

$$\text{Total extract per cent} = \frac{\text{wt. of extract}}{\text{wt. of specimen}} \times 100$$

### ALCOHOLIC POTASH EXTRACT

**Reagents** **Alcoholic Potash Solution**—A 1 *N* alcoholic KOH solution is prepared by dissolving the correct amount of KOH in specially purified ethanol. The ethanol is purified by dissolving 10 g of  $\text{AgNO}_3$  in 3 ml water and adding to 1 liter of ethanol (ethanol denatured with 10% by volume of methanol may be used). Dissolve 3 g of KOH in the smallest amount of water, cool, add it to the  $\text{AgNO}_3$  ethanol solution and shake thoroughly. Allow the solution to stand at least 24 hours, filter and distill.

**Procedure**—Remove the specimen remaining after the chloroform extract or total extract from its wrapping material while wet with solvent and dry the rubber at  $70 \pm 5^\circ\text{C}$  to remove the solvent. Transfer to a 200 ml Erlenmeyer flask, add 50 ml of alcoholic potash solution and heat under a reflux condenser for 4 hours. In the case of hard rubber continue the heating for 16 hours or more. Filter into a 250 ml beaker, wash with two 25 ml portions of boiling alcohol and then with three 25 ml portions of boiling water and evaporate the filtrate just to dryness. Use about 75 ml of water to transfer the residue to a separatory funnel. Acidify the solution with HCl (1:3), testing with Congo red paper. Extract with four 25 ml portions of ether unless the fourth portion should be colored when the extraction shall be continued until no further quantity can be removed. Unite the ether fractions and wash thoroughly with water until free of acid (two washings are generally sufficient). Filter the ether solution through a plug of previously washed absorbent cotton into a weighed flask and wash the separatory funnel and the cotton plug with ether. Evaporate the ether on a steam bath using a gentle current of filtered air to prevent boiling. Remove the flask from the steam bath just prior to the disappearance of the last traces of solvent and continue the passage of air for 10 minutes. Dry the flask at  $100 \pm 5^\circ\text{C}$  to constant weight, cool and weigh.

Calculation.—Calculate the percentage of alcoholic potash extract as follows:

$$\text{Alcoholic potash extract, per cent} = \frac{\text{wt. of extract}}{\text{wt. of specimen}} \times 100$$

#### UNSAAPONIFIABLE ACETONE EXTRACT

*Procedure.*—Add to the acetone extract obtained from a 2-g. specimen, 50 ml. of a 1 *N* alcoholic KOH solution. Heat on the steam bath under a reflux condenser for 2 hours, remove the condenser, and evaporate to dryness. Transfer to a separatory funnel, using about 100 ml. of water. Extract with 25 ml. of ether. Allow the layers to separate thoroughly; then draw off the water layer. Continue extraction of the water layer with fresh portions of ether, including washing out the original flask with a portion, until no more unsaponifiable matter is removed. This usually requires about four washings. Unite the ether layers and wash with water until a negative test for alkali with phenolphthalein is obtained on the wash water. Transfer the ether to a weighed flask and distill off the ether on a steam bath using a gentle stream of filtered air to prevent boiling. Continue the air stream for 5 minutes after the ether is distilled off. Dry the extract to constant weight at  $100 \pm 5^\circ\text{C}$ . and weigh. Save the residue for determination of waxy hydrocarbons and mineral oil.

Calculation.—Calculate the percentage of unsaponifiable acetone extract as follows:

$$\text{Unsaponifiable acetone extract, per cent} = \frac{\text{wt. of extract}}{\text{wt. of specimen}} \times 100$$

#### WAXY HYDROCARBONS

*Procedure.*—To the unsaponifiable matter obtained in the method for Unsaponifiable Acetone Extract, add 50 ml. of absolute ethanol and heat on the steam bath for 30 min. Let the flask stand in a mixture of ice and salt kept at  $-5^\circ\text{C}$ . for at least 1 hour. Filter off the separated waxy hydrocarbons on filter paper by applying gentle suction while keeping the filter funnel surrounded by a salt-ice mixture at  $-5^\circ\text{C}$ . or lower. Wash the precipitate with ethanol (95 to 100%) that has been cooled to  $-5^\circ\text{C}$ . or lower in an ice-salt mixture. Save the filtrate and washings for determination of mineral oil.

Dissolve the precipitate from the filter paper with hot chloroform, and catch the solution in a weighed 100- to 150-ml. beaker. Wash the flask with hot chloroform and add the washings to the solution in the beaker in order to include any insoluble matter adhering to the walls of the flask. Evaporate the solvent on a steam bath, passing a gentle current of filtered air over the residue for 5 minutes after the solvent is essentially evaporated. Dry to constant weight at  $100 \pm 5^\circ\text{C}$ ., cool, and weigh.

Calculation.—Calculate the percentage of waxy hydrocarbons as follows:

$$\text{Waxy hydrocarbons, per cent} = \frac{\text{wt. of waxy hydrocarbons}}{\text{wt. of specimen}} \times 100$$

#### MINERAL OIL

*Procedure.*—Evaporate the alcohol filtrate from the waxy hydrocarbon determination, using a gentle current of filtered air to prevent boiling, add 25 ml. of  $\text{CCl}_4$ ,

and transfer to a separatory funnel. Shake with  $\text{H}_2\text{SO}_4$ , drain off the colored acid, and repeat with fresh portions of  $\text{H}_2\text{SO}_4$  until there is no longer any discoloration. After drawing off all of the  $\text{H}_2\text{SO}_4$ , add a portion of water and sufficient ether to form the ether  $\text{CCl}_4$  layer above the water and wash repeatedly with water until all traces of acid are removed as shown by methyl red indicator test on the water layer. Transfer the ether  $\text{CCl}_4$  layer to a weighed flask and evaporate the solvent on a steam bath using a current of filtered air to prevent boiling. Remove from the steam bath just prior to the disappearance of the last traces of solvent and continue the flow of air for 10 minutes. Dry to constant weight in an air bath at  $100 \pm 5^\circ\text{C}$ , cool and weigh.

**Calculation**—Calculate the percentage of mineral oil as follows

$$\text{Mineral oil per cent} = \frac{\text{wt of residue}}{\text{wt of specimen}} \times 100$$

### SULFUR DETERMINATION

**Definitions** **Free Sulfur**—Free sulfur in a rubber compound is defined as that sulfur which is determined by extraction with  $\text{Na}_2\text{SO}_3$  solution followed by determination of the resulting  $\text{Na}_2\text{S O}_3$  according to the Free Sulfur (Sodium Sulfite) method on page 2209. This determination may include some sulfur in organic compounds and coordinately bound sulfur in some instances. The method is not applicable to IIR rubbers.

**Free Sulfur Acetone Extract**—This is the sulfur removed by acetone extraction (page 2106) or total extract procedure (page 2204) and includes not only elemental sulfur but sulfur in soluble organic compounds. The method is not applicable to NBR or IIR rubbers because of the extraction procedure used. The method is described on page 2209.

**Organic Sulfur**—The organic sulfur consists of any sulfur excluding inorganic sulfides or sulfates remaining in the rubber compound *after acetone extraction or total extraction* has been made. It is not intended to represent the sulfur of vulcanization though it includes any of the following materials: (1) sulfur combined with rubber; (2) sulfur present in accelerators not removed by the extraction procedures; (3) part of the sulfur present in rubber substitutes such as factice and mineral rubber.

The organic plus inorganic sulfur is determined on the extracted sample according to the Zinc Nitric Acid Method on page 2210 in the absence of acid soluble barium salts, antimony or lead compounds and according to the Fusion Method on page 2211 if any of these compounds is present.

The organic sulfur is calculated by subtracting the inorganic sulfur (see below) from the value obtained by this method. The method is not applicable to NBR or IIR rubber because of the extraction procedure used.

**Inorganic Sulfur**—The inorganic sulfur consists of sulfur originally added to the rubber but which has become combined with the fillers during vulcanization and sulfur that is determined as inorganic sulfides or sulfates. The method is described on page 2211 and is applicable only to rubbers for which the acetone extract and total extract procedures are valid.

**Total Sulfur**—This consists of the total organic sulfur present in the *unextracted* sample and is determined as described on pages 2210–2212 according to the definition of organic sulfur.

The above definitions are based on those given in ASTM Designation D297-61T<sup>16</sup> and the procedures are essentially those of this Designation.

#### FREE SULFUR (SODIUM SULFITE) METHOD

*Apparatus.*—400 ml. thin wall, chemically resistant glass flask; Büchner funnel.

*Reagents.* Sodium Sulfite ( $\text{Na}_2\text{SO}_3$ ) Solution, 50 g. per l.

Sodium Stearate Suspension, 1 g. per l.

Paraffin.

Strontium Chloride ( $\text{SrCl}_2$ ) Solution, 5 g. per l.

Cadmium Acetate [ $(\text{CH}_3\text{COO})_2\text{Cd}$ ] Solution, 30 g. per l.

Formaldehyde Solution, 40%.

Acetic Acid, Glacial.

Starch Solution, 10 g. per l.

Iodine Solution, 0.05 to 0.1 *N*.

*Procedure.*—Place 2 g. of a sample thinly sheeted (0.05 to 0.075 cm. (0.02 to 0.03 in.)) in a 400-ml., thin-wall, chemically resistant glass flask. Add 100 ml. of  $\text{Na}_2\text{SO}_3$  solution, 5 ml. of a sodium stearate suspension in water, and approximately 1 g. of paraffin. Cover the flask with a small watch glass and heat so as to boil gently for 4 hours, or digest just below the boiling point for 16 hours. Remove the flask and add 100 ml. of  $\text{SrCl}_2$  solution and 10 ml. of cadmium acetate solution. Separate the rubber and precipitates by filtration, using a Büchner funnel with suction. (The funnels are prepared by forming a thin asbestos pad, or a thicker layer of diatomaceous earth filter-aid, over a single sheet of qualitative filter paper. Filters thus prepared can be used numerous times.) Wash with two 75- to 100-ml. portions of a wash solution containing 40 ml. of cadmium acetate solution per liter of wash solution. To the filtrate, add while stirring 10 ml. of 40% formaldehyde solution, 10 ml. of glacial acetic acid, and 5 ml. of starch solution. Add enough crushed ice to bring the temperature of the solution below 15°C., and titrate with iodine solution to a blue end point.

*Blank.*—Run a blank determination on the reagents, and subtract this figure, usually 0.2 to 0.3 ml., from the titrations on the samples.

*Calculation.*—Calculate the percentage of free sulfur as follows:

$$\text{Free sulfur, per cent} = \frac{(A - B)N \times 0.032}{C} \times 100$$

where *A* = ml. of iodine solution required for titration of the sample,

*B* = ml. of iodine solution required for titration of the blank,

*N* = normality of the iodine solution, and

*C* = g. of sample used.

#### FREE SULFUR, ACETONE EXTRACT

*Reagents.* Zinc-Nitric Acid Solution, see page 2210.

*Procedure.*—Add to the flask containing the acetone extract, 10 ml. of  $\text{Zn-HNO}_3$  solution and 2 to 3 ml. of bromine and cover with a watch glass. Allow to stand near a steam plate for 30 min., then heat on the steam plate to a foamy syrup. Add 10 ml. of fuming  $\text{HNO}_3$  and heat on the hot plate with the cover removed until all the bromine is expelled. Continue the determination as described in the procedure for the Zinc-Nitric Acid Method (page 2210) after the evaporation of the bromine.



## SULFUR ZINC NITRIC ACID METHOD

**Reagents** Zinc Nitric Acid Solution [add 200 g zinc oxide (ZnO) to 1 liter of nitric acid ( $\text{HNO}_3$ ) (sp gr 1.42)]

Fuming Nitric Acid ( $\text{HNO}_3$ )

Bromine Water

Hydrochloric Acid Solution (HCl), 1.6 m water

Picric Acid Solution saturated

Barium Chloride ( $\text{BaCl}_2$ ) Solution 100 g per l

**Procedure**—Place 0.5 g of soft rubber or 0.2 g of hard rubber (extract the specimen with acetone or acetone-chloroform mixture if organic sulfur is to be determined) in a 500 ml Erlenmeyer destruction flask of chemically resistant material. Add 10 ml of Zn- $\text{HNO}_3$  solution and moisten the sample thoroughly. Let stand at least 1 hour overnight if convenient. By so doing the sample becomes partly decomposed; this permits the addition of fuming  $\text{HNO}_3$  with no danger of ignition of the sample. Add 15 ml of fuming  $\text{HNO}_3$  and whirl the flask rapidly to keep the sample immersed to avoid ignition. With some samples it may be necessary to cool the flask under running water.

When the solution of the rubber appears to be complete, add 5 ml of a saturated water solution of bromine and slowly evaporate the mixture to a foamy syrup. (For the determination of sulfur in unvulcanized mixtures use 3 ml of bromine in place of bromine water.)

If organic matter or carbon remain at this point, add a few milliliters of fuming  $\text{HNO}_3$  and a few crystals of  $\text{KClO}_3$  (*Caution*) and evaporate at a boil. Repeat this operation until all carbon is gone and the solution is clear, colorless or light yellow.

At this point either of the following procedures may be used.

**Procedure A**—Place the flask on an asbestos gauze and evaporate the mixture to dryness over a Tirrill burner. Then bake the mixture at the highest temperature of the burner until all nitrates are decomposed and no more nitrogen oxide fumes can be detected. The flask must be carefully annealed after this procedure by gradually decreasing the flame or by placing the flask on successively cooler sources of heat.

**Procedure B**—Evaporate the mixture, cool, add 10 ml of HCl and evaporate to dryness, avoiding spattering. Repeat this procedure once or more than once if oxides of nitrogen are still evolved.

Cool the flask, add 50 ml of HCl (1.6) and digest hot until solution is as complete as possible. Filter while hot. Wash the filter and dilute the filtrate and washings to about 300 ml. Add 10 ml of saturated picric acid solution, heat to  $90^\circ\text{C}$  and precipitate the sulfate by dropwise addition of  $\text{BaCl}_2$  solution while stirring vigorously. Digest the precipitate overnight, preferably at 60 to  $80^\circ\text{C}$ , using a watch glass to cover the beaker. Filter the  $\text{BaSO}_4$  and wash with water until the filter is colorless. Dry ash and finally ignite the precipitate at 600 to  $900^\circ\text{C}$  to constant weight. Cool in a desiccator and weigh.

**Calculation**—Calculate the percentage of sulfur as follows:

$$\text{Sulfur, per cent} = \frac{\text{wt of BaSO}_4 \times 0.1373}{\text{wt of specimen}} \times 100$$

*SULFUR, FUSION METHOD*

**Reagents.** Nitric Acid-Bromine Solution [add a considerable excess of bromine to nitric acid ( $\text{HNO}_3$ ) (sp. gr. 1.42) so that a layer of bromine is present in the reagent bottle. Shake thoroughly and allow to stand 24 hours before using.]

Sodium Carbonate ( $\text{Na}_2\text{CO}_3$ ) Solution, 50 g. per l.

**Procedure.**—Place 0.5 g. of soft rubber or 0.2 g. of hard rubber in a porcelain crucible of about 75-ml. capacity. The sample shall have been extracted with acetone or acetone-chloroform mixture if organic plus inorganic sulfur is to be determined. Add 15 ml. of the  $\text{HNO}_3$ — $\text{Br}_2$  mixture, cover the crucible with a watch glass, and let it stand for 1 hr. in the cold. Heat for 1 hr. on the steam bath, remove the cover, rinse it with a little water, and evaporate to dryness.

Add 3 ml. of  $\text{HNO}_3$ , cover, warm a short time on the steam bath, then allow to cool. Carefully add in small portions, by means of a glass spatula, 5 g. of  $\text{Na}_2\text{CO}_3$  (weighed to 0.5 g.). Raise the watch glass only high enough to permit the introduction of the spatula. Allow the  $\text{Na}_2\text{CO}_3$  to slide down the side of the crucible, as it must not be dropped directly into the acid. Rinse the watch glass with 2 or 3 ml. of hot water and stir the mixture thoroughly with a glass rod. Digest for a few minutes, spread the mixture halfway up the side of the crucible to facilitate drying, and dry on a steam bath. Fuse the mixture by heating over a sulfur-free flame.

Place the crucible in an inclined position on a wire triangle and start the ignition over a low flame. The tendency for the organic matter to burn too briskly may be controlled by judicious use of the stirring rod with which the burning portion is scraped away from the rest. When part of the mass is burned white, work a fresh portion into it until all of the organic matter is destroyed. It is necessary to hold the edge of the crucible with tongs. Toward the last half of the operation the flame should be increased. It is unnecessary to heat the crucible to redness. With care, a crucible can be used for at least 10 to 12 fusions.

After a fusion, allow the crucible to cool. Place it in a 400-ml. beaker, add sufficient water to cover the crucible (about 125 ml.), and digest on the steam bath or plate for at least 2 hours.

Filter the solution into a covered 400-ml. beaker containing 5 ml. of  $\text{HCl}$  and wash the residue thoroughly with hot  $\text{Na}_2\text{CO}_3$  solution (50 g. per l.). A qualitative test for barium may be made on the residue, but no analysis for barium or correction because of its presence is necessary, unless a detailed ash analysis is desired. Acidify the filtrate to indicator paper with  $\text{HCl}$  and add 2 ml. in excess. Precipitate barium sulfate and complete the determination as described in Zinc-Nitric Acid Method, page 2210.

Calculation.—Calculate the percentage of sulfur as follows:

$$\text{Sulfur, per cent} = \frac{\text{wt. of BaSO}_4 \times 0.1373}{\text{wt. of specimen}} \times 100$$

*SULFUR, INORGANIC, ANTIMONY ABSENT*

**Procedure.**—Extract a 1.0 g. specimen with acetone or with acetone-chloroform mixture. Dry the sample, place in a porcelain crucible of about 75-ml. capacity, and distill off the rubber in a muffle furnace, using a maximum temperature of  $150^\circ\text{C}$ . A burner may be used for ashing if the sample is not allowed to catch fire.

A wire gauze under the crucible will aid in preventing combustion. The carbon need not be completely burned off in this ignition. If acid soluble barium salts or lead are absent add 3 ml of  $\text{HNO}_3\text{-Br}_2$  mixture to the ash cover with a watch glass and heat for 1 hour. Transfer the contents of the crucible with washing into a 500 ml Erlenmeyer destruction flask of chemically resistant material and evaporate to dryness. Proceed with the determination of sulfur as in the Zinc Nitric Acid Method page 2210. In the presence of acid soluble barium salts or lead determine the sulfur by treating the ash according to the Fusion Method page 2911.

**Calculation**—Calculate the percentage of inorganic sulfur as follows

$$\text{Inorganic sulfur per cent} = \frac{\text{wt of BaSO}_4 \times 0.1373}{\text{wt of specimen}} \times 100$$

## TOTAL INORGANIC FILLERS

### FILLERS RUBBER SOLVENT METHOD<sup>18</sup>

**Scope**—This method is intended for use in determining the fillers in rubber compounds containing decomposable fillers. It is not applicable to nitrile type synthetic rubber compounds nor to any synthetic rubber compound that will not dissolve in the solvent oil nor to hard rubber compounds.

Solvents for vulcanized rubber have been suggested from time to time in attempts to isolate the compounding ingredients in rubber goods by methods that would avoid the thermal decomposition incident to the ash method. Aniline, terrene, kerosene, toluene, and cymene have been used with success. For the most part filtration is slow with these solvents. The method consists of dissolving the rubber compound in the solvent, separating the inorganic residue and some organic residue by filtration and weighing the residue. A correction is made for the organic material and free carbon by removing the decomposable ingredients from the inorganic residue with HCl and determining the organic portion of the residue by ignition.

In the procedure the rubber solvent consists of a mixture of 300°C mineral seal oils from two or more sources. Before use the mixed oils are passed through a column of fuller's earth contained in a glass tube 3 ft in length and 1½ in in diameter. The filtered mixture is practically colorless. The rubber hydrocarbon in vulcanized soft rubber compounds is dissolved by the solvent in about 2 hours at 150 to 160°C. The subsequent operations incident to isolating the compounding ingredients are conducted as readily as with an aqueous solution. The solvent is recommended because of completeness of separation and the rapidity with which it may be filtered. It has been determined empirically that the colloidal solution of rubber formed does not have the disadvantage of slow filtration which is typical of some other solvents of vulcanized rubber.

After the mixture of mineral oils has acted on a rubber compound the rubber is dissolved and the fillers remain for some time in suspension in the solution. On continued heating the fillers settle to the bottom of the container. In mixtures of asbestos fibers and rubber compound such as are present in compressed asbestos sheet packing it is possible by the above difference in behavior to separate the rubber and rubber compound ingredients from the asbestos fibers. While the

<sup>18</sup> Tentative Methods for Chemical Analysis of Rubber Products ASTM Designation D297-59T

fillers are still in suspension the solution is poured through a sieve, which retains the fibers. A No. 80 (177-micron) sieve is recommended for the purpose. Subsequently, by continued heating the rubber and compounding ingredients may be separated. Any asbestos present as asbestine is separated with the compounding ingredients. In the case of rubber goods prepared from new rubber, a small amount of undissolved material is obtained for which a correction must be made.

*Apparatus.*—Assay flask, 150 ml.; Gooch crucible.

*Reagents.* Rubber Solvent.—The mineral oil used in the solution method of determining rubber and fillers should have approximately the following properties:

Saybolt	
Universal	{ at 68°F. (20°C.)..... 56 sec.
viscosity	{ at 100°F. (38°C.)..... 45 sec.
Flash point.....	270°F. (132°C.)
Fire point.....	350°F. (177°C.)
Specific gravity.....	0.853
Color.....	colorless

*Procedure.*—Weigh a 0.5- to 0.6-g. specimen. Extract with acetone-chloroform mixture (page 2205) for a minimum of 8 hours. If the extracting liquid is still colored at the end of this time, continue the extraction until the liquid is clear in the siphon cup. Remove the specimen and place it in a 150-ml. lipped assay flask. Add 20 to 25 ml. of the solvent oil, cover with a watch glass and heat in an air bath at a temperature of 150 to 165°C. until solution appears complete, and then continue heating for 15 to 30 minutes. Solution may be considered complete when the rubber colloid has been broken down and the oil seems quite clear. Remove the flask from the air bath, cool to about 80°C., and add in a small stream 10 to 15 ml. of benzene while mixing thoroughly. Allow to cool and then dilute with sufficient petroleum ether to fill the flask to within about 2 cm. of the top. Mix thoroughly, cover the flask to prevent evaporation, and allow the mixture to stand until the particles settle.

Prepare a Gooch crucible with finely divided asbestos that previously has been treated with strong NaOH solution and HCl and washed well with water. Ignite the crucible, cool, and weigh; call this weight *c*. Filter the mixture by decantation through the crucible, using suction. Wash well with petroleum ether, followed by warm acetone, and by a warm mixture of equal volumes of acetone and chloroform if the filtrate is dark. Remove as much as possible of the organic residue by washing; finally, wash with hot alcohol. A portion of the fillers will remain in the flask. Dry the crucible and flask with their contents for 1 hour at a temperature of 105 to 110°C. Cool, and weigh. Call the weight of the flask and contents *d*, and the weight of the crucible and contents *e*. For inorganic sulfur determination or for BaCO<sub>3</sub> determination do not perform the weighings, but refer to pages 2211 and 2220.

Remove the acid-soluble compounding ingredients from the flask and Gooch crucible in the following manner: Place the crucible in the filter funnel and then add a few milliliters of boiling alcohol to the flask and crucible. Allow to soak for 2 or 3 minutes and then wash two or three times with boiling water. Let the flask cool. Add 10 ml. of HCl and swirl the flask to bring the acid in contact with the compounding ingredients. Pour the acid from the flask into the crucible and let it stand until no more bubbles rise through the liquid. If carbonates are

present there is danger of loss by excessive frothing. This can be prevented by first adding a few drops of the HCl to the crucible and sucking it through the pad. After the violent action has ceased add the remainder of the 10 ml of HCl. When no more gas is evolved, draw the HCl through the pad and again wash with 20 ml of HCl adding a little at a time. Wash well with hot water, and completely transfer the residue remaining in the flask to the asbestos pad. Dry the flask and crucible for 1 hour at 105°C, cool and weigh. Call the weight of the flask  $f$ , and that of the crucible containing the organic residue and acid insoluble fillers  $h$ . Burn the organic residue from the asbestos pad by igniting in a furnace at 700°C, cool, and weigh. Call this weight  $k$ .

**Calculation**—Calculate the percentage of fillers as follows

$$\text{Fillers per cent} = \frac{100[(e + d + k) - (c + f + h)]}{\text{wt of specimen}}$$

### ASH

The total ash determination of rubber compounds may be carried out as described for natural rubber page 2151 of this chapter. However, a slower method is recommended by ASTM<sup>16</sup> for referee use. This procedure is as follows.

**Apparatus**—An electric muffle furnace shall be employed for the test. Numbered porcelain crucibles 41 mm in diameter and 25 mm in height shall be used. The bottom of the furnace shall be covered by a sheet of asbestos 0.06 in in thickness cut to fit.

**Procedure** Extract a 2 g specimen with acetone as described in the acetone extraction (page 2156). Allow the extracted specimen to dry at 100°C, cool in a desiccator, and weigh. Divide the specimen into two parts of equal weight and

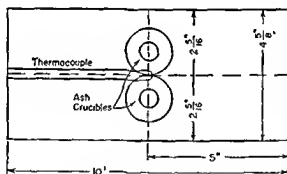


FIG 43.5 Location of Apparatus for Ash Determination (Referee Method)

place each of them in crucibles previously ignited, cooled in a desiccator, and weighed. Place the two crucibles, with contents, together (with their tops touching) in the furnace on a line crossing the furnace halfway between its ends as shown in Fig 43.5. Regulate the temperature of the furnace by means of a rheostat so that the temperature corresponds to the curve shown in Fig 43.6, with a maximum permissible variation of plus or minus 25°C. Measure the temperature with a thermocouple (previously calibrated) enclosed in a quartz tube closed at one end 6 to 7 mm in diameter, 0.5 to 1 mm in thickness, and placed in a horizontal position in contact with the asbestos sheet on the bottom of the furnace, so that the

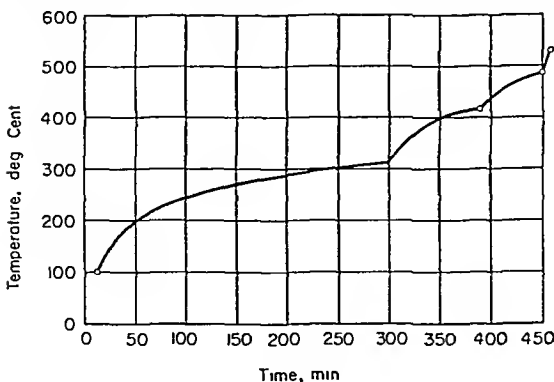


FIG. 43-6. Time-Temperature Curve for Ash Determination (Referee Method).

hot junction of the couple is on a line crossing the furnace halfway between its ends, and halfway between the two crucibles, as shown in Fig. 43-5. Adjust the door of the furnace to conform to the following requirements:

	Opening
First 400 minutes	.. $\frac{1}{2}$ in.
From 400 to 450 minutes	.. $1\frac{1}{2}$ in.
Remainder of period (7 minutes)	.. wide open

At the end of the period of heating, as shown, remove the crucibles from the furnace, cool in a desiccator, and weigh.

Calculation.—Calculate the percentage of ash as follows:

$$\text{Ash, per cent} = \frac{\text{wt. of ash}}{\text{wt. of sample}} \times 100$$

This total ash may be considered as a measure of the non-organic fillers in the compound.

## ANALYSIS OF ASH

### SILICON DIOXIDE AND INSOLUBLE MATTER

*Procedure.*—Dissolve one of the specimens of ash in 10 ml. of HCl, rinse the crucible thoroughly, dilute to 100 ml., and evaporate to dryness in a casserole. Bake for 1 hour at 110°C. Moisten with 10 ml. of HCl and 3 drops of HNO<sub>3</sub>, and digest for 15 minutes on the steam bath. Add 100 ml. of water, boil, filter, and wash with hot water. Dry and ignite in a porcelain crucible. Weigh to determine the SiO<sub>2</sub> and insoluble matter. If the residue is large enough to justify an analysis for SiO<sub>2</sub>, transfer to a platinum crucible and add 2 to 3 ml. of HF and a few drops of H<sub>2</sub>SO<sub>4</sub>. Evaporate to dryness, and carefully ignite at a low red heat. The loss in weight is SiO<sub>2</sub>.

Calculation.—Calculate the percentages of SiO<sub>2</sub>, and of SiO<sub>2</sub> and insoluble matter as follows:

$$\text{SiO}_2 \text{ and insoluble matter, per cent} = \frac{A - B}{C} \times 100$$

$$\text{SiO}_2 \text{ per cent} = \frac{(A - B) - (D - E)}{C} \times 100$$

where  $A$  = weight of residue and porcelain crucible after ignition,

$B$  = weight of porcelain crucible,

$C$  = weight of original specimen,

$D$  = weight of residue and platinum crucible after treatment with HF and ignition and

$E$  = weight of platinum crucible

A large residue after the HF treatment may be  $\text{BaSO}_4$ ,  $\text{PbSO}_4$ ,  $\text{TiO}_2$  which may be identified by microscopic examination. If small amounts of  $\text{Al}_2\text{O}_3$  and  $\text{Fe}_2\text{O}_3$  are present in the residue they may be dissolved by fusion with  $\text{K}_2\text{S}_2\text{O}_8$  reprecipitated with  $\text{NH}_4\text{OH}$  and added to the  $\text{R}_2\text{O}_3$  precipitate provided  $\text{TiO}_2$  is absent and an exact analysis for  $\text{Al}_2\text{O}_3$ ,  $\text{Fe}_2\text{O}_3$  or both is desired.

### LEAD OXIDE

**Procedure**—A complete precipitation of the lead as  $\text{PbS}$  may be made if the concentration and acidity are carefully controlled. Just neutralize the filtrate from the determination of  $\text{SiO}_2$  and insoluble matter with  $\text{NH}_4\text{OH}$  and add 1 ml of  $\text{HCl}$ . Run a rapid stream of  $\text{H}_2\text{S}$  into the solution and dilute to between 50 and 100 ml. Continue the addition of  $\text{H}_2\text{S}$  until precipitation is complete. Filter and wash with a saturated solution of  $\text{H}_2\text{S}$ . If antimony is present it will precipitate under these conditions; zinc may also be precipitated but neither will interfere with the determination of lead. Dissolve the  $\text{PbS}$  in  $\text{HNO}_3$  (1:1) boil to complete solution. If antimony is present it may not be dissolved by this procedure. Filter. Cool the filtrate add 10 ml of  $\text{H}_2\text{SO}_4$  and evaporate to dense white fumes of  $\text{H}_2\text{SO}_4$ . Cool dilute with 50 ml of water add an equal volume of ethanol (90%) and let stand overnight. Filter on a tared Gooch crucible, wash with ethanol (50%) and dry at  $105^\circ\text{C}$ .

**Calculation**—Calculate the percentage of lead as follows

$$\text{Lead oxide per cent} = \frac{(A - B) \times 0.7670}{C} \times 100$$

where  $A$  = weight of crucible and  $\text{PbSO}_4$ ,

$B$  = weight of crucible,

$C$  = weight of original specimen, and

0.7670 = conversion factor from  $\text{PbSO}_4$  to  $\text{PbO}$

### IRON AND ALUMINUM OXIDES

**Procedure**—Boil the filtrate from the lead sulfide precipitation to expel  $\text{H}_2\text{S}$ . Adjust the volume of solution to 100 to 150 ml. Add a few drops of  $\text{HNO}_3$  and boil the solution again. Test for ferrous iron, using  $\text{K}_3\text{Fe}(\text{CN})_6$  as an outside indicator on a spot plate. If ferrous iron is present, add more  $\text{HNO}_3$  and proceed as before until all the iron is oxidized. Add 5 g of solid  $\text{NH}_4\text{Cl}$ . Add  $\text{NH}_4\text{OH}$  until the solution is colored definitely yellow by methyl red but do not add an excess. Heat to boiling and boil for 5 minutes. When the precipitate has settled

filter, with the aid of filter pulp if the precipitate is large, and wash with  $\text{NH}_4\text{Cl}$  (20 g. per l.). Carefully char off the filter paper at *low* temperature and ignite the residue in a freely oxidizing atmosphere.

Calculation.—Calculate the percentage of  $\text{R}_2\text{O}_3$  as follows:

$$\text{R}_2\text{O}_3, \text{ per cent} = \frac{(A - B)}{C} \times 100$$

where  $A$  = weight of crucible and  $\text{R}_2\text{O}_3(\text{Fe}_2\text{O}_3 + \text{Al}_2\text{O}_3)$ ,

$B$  = weight of crucible, and

$C$  = weight of original specimen.

Iron in the  $\text{R}_2\text{O}_3$  residue may be determined, if desired, by fusing the residue with potassium pyrosulfate, dissolving the melt in 6  $N$   $\text{H}_2\text{SO}_4$ , reducing the iron with amalgamated zinc, and titrating the iron with  $\text{KMnO}_4$  solution.

### CALCIUM OXIDE

*Procedure.*—If acid-soluble barium salts were found to be absent, dilute the filtrate from the  $\text{R}_2\text{O}_3$  determination to 200 ml., add methyl red indicator, and neutralize with 1  $N$   $\text{H}_2\text{SO}_4$ . Add 25 ml. of formic acid mixture (200 ml. formic acid, 770 ml. water, 30 ml.  $\text{NH}_4\text{OH}$ ). If acid-soluble barium salts were found to be present, remove the barium as follows: Dilute the filtrate from the  $\text{R}_2\text{O}_3$  determination to 200 ml., neutralize with 6  $N$   $\text{HCl}$ , and add 10 ml., in excess. Heat to boiling. Add 1  $N$   $\text{H}_2\text{SO}_4$  to precipitate barium, but avoid a large excess. Digest until the precipitate settles, test for completeness of precipitation, and digest for at least 2 hours or until the precipitate is filterable. Filter, wash, and discard the precipitate. Concentrate the filtrate to 200 ml., neutralize with  $\text{NH}_4\text{OH}$  to methyl red indicator, neutralize with 1  $N$   $\text{H}_2\text{SO}_4$ , and add 25 ml. of formic acid mixture.

Proceed at this point to remove zinc by heating the solution to  $60^\circ\text{C}$ . and saturating with  $\text{H}_2\text{S}$  for 20 minutes. Digest for 1 hour at  $60^\circ\text{C}$ ., filter, and wash with formic acid wash solution (30 ml. formic acid mixture diluted to 1 liter and saturated with  $\text{H}_2\text{S}$ ). Test for complete removal of zinc with  $(\text{NH}_4)_2\text{S}$  in alkaline solution. Filter again if necessary. Make the filtrate just acid with 6  $N$   $\text{HCl}$ , and evaporate to 150 ml. Filter to remove sulfur. Add methyl red indicator, heat to  $50^\circ\text{C}$ ., neutralize with  $\text{NH}_4\text{OH}$ , and add 1 ml. in excess. Make the solution just acid with oxalic acid solution (100 g. per l.), add 12 ml. in excess, and boil for 2 min., while stirring vigorously. Add approximately 50 ml. of saturated ammonium oxalate solution, adding more if the solution is still acid to methyl red, dilute to 250 to 300 ml., boil for 2 minutes, and digest on a steam bath for 1 hour. Allow to cool, filter, and wash with a solution containing 2 g. of ammonium oxalate and 1 g. of oxalic acid per liter. Dissolve the precipitate in 50 ml. of warm 3  $N$   $\text{HCl}$  and reprecipitate by the above procedure, uniting filtrate and washings with the first filtrate and washings. The quantities of oxalic acid and ammonium oxalate used in the reprecipitation may be one-half or possibly only one-fourth as large as in the first precipitation. If  $\text{CaO}$  is to be determined volumetrically, wash the precipitate of  $\text{CaC}_2\text{O}_4$  finally with water, dissolve the precipitate from the paper in hot 6  $N$   $\text{H}_2\text{SO}_4$ , and titrate hot with standard 0.1  $N$   $\text{KMnO}_4$ , finally adding the filter paper to the mixture and finishing the titration rapidly. A sintered glass crucible of fine porosity may be advantageously substituted for the filter paper. If  $\text{CaO}$  is to be determined gravimetrically, dry and ignite the precipitate in a covered porcelain crucible, the ignition temperature being from 1000 to  $1200^\circ\text{C}$ .



Calculations—Calculate the percentage of CaO as follows

*Volumetric Method—*

$$\text{CaO per cent} = \frac{A \times V \times 0.028}{C} \times 100$$

where  $A$  = milliliters of  $\text{KMnO}_4$  solution

$V$  = normality of  $\text{KMnO}_4$  solution,

$C$  = weight of original specimen and

0.028 = grams of CaO equivalent to each milliliter of exactly 1  $N$   $\text{KMnO}_4$  solution

*Gravimetric Method—*

$$\text{CaO per cent} = \frac{A - D}{C} \times 100$$

where  $A$  = weight of precipitate plus crucible,

$D$  = weight of crucible and

$C$  = weight of original specimen

### MAGNESIUM OXIDE

**Procedure** Evaporate to dryness the combined filtrates and washings from the determination of calcium. Add 50 ml of  $\text{HNO}_3$ , cover and warm until the evolution of gas subsides. Uncover and evaporate to dryness avoiding spattering. Heat the residue on a hot plate for 2 to 3 hours overnight if convenient. Dissolve the residue in 100 ml of water slightly acidify with  $\text{HCl}$  and add 25 ml of  $(\text{NH}_4)\text{HPO}_4$  (100 g per l). Cool to  $15^\circ\text{C}$  (preferably use an ice bath) neutralize very slowly with  $\text{NH}_4\text{OH}$  while stirring constantly using methyl red as an indicator and add 10 ml of  $\text{NH}_4\text{OH}$  in excess. Let the solution stand overnight filter without attempting to transfer the precipitate and wash with 1  $\%$   $\text{NH}_4\text{OH}$ . Dissolve the precipitate in warm 3  $\%$   $\text{HCl}$  using the beaker from which the precipitate was filtered. Dilute to 100 ml add 5 ml of  $(\text{NH}_4)\text{HPO}_4$  (100 g per l) neutralize very slowly with  $\text{NH}_4\text{OH}$  while stirring constantly and add 5 ml of  $\text{NH}_4\text{OH}$  in excess. Let stand for at least 4 hours then filter through paper or asbestos which is known not to be affected by ignition with alkaline phosphates. If paper is used it must be charred off at very low temperatures to prevent fireproofing of the paper. Ignite to  $\text{Mg}_2\text{P}_2\text{O}_7$  at 1000 to  $1200^\circ\text{C}$  for 60 minutes and weigh.

Calculation—Calculate the percentage of  $\text{MgO}$  as follows

$$\text{MgO per cent} = \frac{(A - B) \times 0.3621}{C} \times 100$$

where  $A$  = weight of crucible and precipitate,

$B$  = weight of crucible,

$C$  = weight of original specimen, and

0.3621 = conversion factor from  $\text{Mg}_2\text{P}_2\text{O}_7$  to  $\text{MgO}$

### ZINC OXIDE

**Procedure**—Dissolve the second sample of ash in 15 ml of  $\text{HCl}$  in a beaker. Remove the crucible from the beaker rinsing it thoroughly. Evaporate the solution to 5 ml and cool. Add 10 ml of saturated bromine water, 5 g of  $\text{NH}_4\text{Cl}$

and 15 ml. of  $\text{NH}_4\text{OH}$ , and boil vigorously for 3 minutes. Filter off the precipitated hydroxides, washing in four portions with 100 ml. of a solution containing 50 g. of  $\text{NH}_4\text{Cl}$  and 25 g. of  $\text{NH}_4\text{OH}$  per liter. Dilute the solution to 250 ml., heat to boiling, and add 4 drops of  $(\text{NH}_4)_2\text{S}$  to destroy oxidizing agents. Neutralize with  $\text{HCl}$ , add 10 ml. in excess, and divide the solution into two approximately equal portions. Titrate one portion at  $75^\circ\text{C}$ . with  $\text{K}_4\text{Fe}(\text{CN})_6$  solution, using a saturated uranyl acetate solution as an outside indicator. The first appearance of a brown coloration on the spot plate indicates the end point. Titrate the first portion by adding 0.5- to 1-ml. increments of  $\text{K}_4\text{Fe}(\text{CN})_6$  solution. Add the second portion of zinc solution to the titrated first portion and continue the titration at  $75^\circ\text{C}$ ., using the first titration as a guide to estimate the total titration. Approach the end point by adding 0.05- to 0.10-ml. increments of  $\text{K}_4\text{Fe}(\text{CN})_6$  solution.

**Standardization and Blanks.**—The potassium ferrocyanide shall be approximately 0.04 *M* (17 g. of  $\text{K}_4\text{Fe}(\text{CN})_6 \cdot 3\text{H}_2\text{O}$  per liter). One milliliter of this solution is equivalent to approximately 5 mg. of  $\text{ZnO}$ . Standardize the  $\text{K}_4\text{Fe}(\text{CN})_6$  solution against zinc of known purity by the same method as used for the determination. Each analyst should run his own standardization because of variations in color sensitivity. Blanks must be run on the standardization and on the analysis.

**Calculation.**—Calculate the percentage of  $\text{ZnO}$  as follows:

$$\text{ZnO, per cent} = \frac{AB}{C} \times 100$$

where *A* = ml. of  $\text{K}_4\text{Fe}(\text{CN})_6$  solution,

*B* = g. of  $\text{ZnO}$  equivalent to each ml. of  $\text{K}_4\text{Fe}(\text{CN})_6$  solution, and

*C* = weight of original specimen.

#### TOTAL BARIUM AS BARIUM SULFATE

**Procedure.**—Analyze the third specimen of ash, which shall have been ashed in a 50-ml. crucible, for total barium as follows: Fuse the specimen with 5 g. of a mixture of equal parts of  $\text{Na}_2\text{CO}_3$  and  $\text{NaNO}_3$ . Stir well during the fusion. Cool the crucible, place it in a 400-ml. beaker with about 125 ml. of water, and digest on the steam plate or bath overnight. Filter the solution and wash the residue well with hot  $\text{Na}_2\text{CO}_3$  solution (50 g. per l.). Wash this residue back into the original beaker with hot water, dissolve the residue in the beaker and any traces on the filter paper with  $\text{HCl}$ , and heat the solution on the steam bath. Filter and wash thoroughly with hot water. Adjust the acidity by means of 6 *N*  $\text{NH}_4\text{OH}$  and 6 *N*  $\text{HCl}$  to be between 0.2 and 0.3 *N* in  $\text{HCl}$ . Cool, saturate the solution with  $\text{H}_2\text{S}$ , and, when the  $\text{PbS}$  has settled, filter into a 400-ml. beaker and wash thoroughly. The total volume of the solution shall not be over 200 ml. Precipitate the barium with  $\text{H}_2\text{SO}_4$  (1:16) and treat the precipitated  $\text{BaSO}_4$  in the usual manner as for sulfur determination.

**Calculations.**—Calculate the percentages of total barium as  $\text{BaSO}_4$  as follows:

$$\text{Total barium as BaSO}_4, \text{ per cent} = \frac{\text{wt. of BaSO}_4}{\text{wt. of specimen}} \times 100$$

#### OTHER FILLERS AND COMPOUND INGREDIENTS

The procedures are those of ASTM Designation D297-61T except where otherwise noted.

## BARIUM CARBONATE

**Scope**—Barium carbonate is determined if the presence of acid soluble barium salts is indicated by preliminary test for Qualitative Nonrubber Constituents page 2203 and if the presence of  $\text{BaSO}_4$  is also indicated by the presence of acid insoluble ash that will give a test for barium after  $\text{Na}_2\text{CO}_3$  fusion. The procedure given is applicable to the synthetic rubbers as well as natural rubber.

**Procedure**—Place a 1 g specimen in a porcelain boat and place this in a combustion tube through which passes a current of  $\text{CO}$ . Ash the sample in the tube. After ignition and cooling in the atmosphere of  $\text{CO}$ , remove the boat, finely grind the residue in an agate mortar, transfer it to a 250 ml beaker and treat with 5 to 10 g of  $(\text{NH}_4)_2\text{CO}_3$ , 15 to 20 ml of  $\text{NH}_4\text{OH}$  and about 50 ml of water. Boil the mixture for 20 minutes, filter and wash the precipitate thoroughly to remove all soluble sulfates. Wash the residue on the filter paper back into the original beaker and add about 10 ml of glacial acetic acid with sufficient water to make the total volume about 100 ml. Heat this to boiling and filter through the same paper as before. Pass  $\text{H}_2\text{S}$  into the filtrate to precipitate the lead. Filter, wash and discard the precipitate. Precipitate the barium with  $\text{H}_2\text{SO}_4$  (1.16) and determine in the usual manner.

**Calculations**—Calculate the percentages of  $\text{BaCO}_3$  and of  $\text{BaCO}_3$  as  $\text{BaSO}_4$  as follows:

$$\text{BaCO}_3 \text{ per cent} = \frac{\text{wt of BaSO}_4 \times 0.8458}{\text{wt of specimen}} \times 100$$

$$\text{BaCO}_3 \text{ as BaSO}_4 \text{ per cent} = \frac{\text{wt of BaSO}_4}{\text{wt of specimen}} \times 100$$

## TOTAL ANTIMONY

**Scope**—Antimony is determined when its presence is indicated in test for Qualitative Nonrubber Constituents page 2203. Since it is determined as the sulfide, the percentage of antimony sulfide will not usually represent the exact weight of the substance as originally compounded. This is so because commercial antimony sulfide normally has some excess sulfur or other impurities present.

**Reagents**—Standard Potassium Bromate Solution (0.1 N). Dissolve approximately 2.79 g of  $\text{KBrO}_3$  in 1 liter of water (NOTE). Standardize this solution by means of standard arsenious oxide as follows. Use a sample containing from 0.1 to 0.2 g of  $\text{As}_2\text{O}_3$ . Dissolve it in  $\text{KOH}$ , neutralize with  $\text{HCl}$  and add 15 ml of  $\text{HCl}$  in excess. Dilute to 100 ml, warm to about 60 C, and titrate with  $\text{KBrO}_3$  using two drops of methyl red solution (0.2%) as indicator. When the indicator fades, add the  $\text{KBrO}_3$  slowly, using more indicator if desired. At the end point the solution turns colorless and an added drop of indicator should be decolorized.

$$\text{Sb equivalent of 1 ml of KBrO}_3 = \frac{\text{wt of As}_2\text{O}_3 \times 1.23}{\text{milliliters of KBrO}_3}$$

**NOTE**—Potassium bromate of known purity may be used as a primary standard for making this solution. Both the solid and the solution are very stable. If  $\text{KBrO}_3$  is used as a primary standard, 1 ml of 0.1 N  $\text{KBrO}_3$  is equivalent to 0.006089 g of antimony.

**Procedure**—Weigh out a 0.5 g sample and transfer to a Kjeldahl flask. Add 25 ml of  $\text{H}_2\text{SO}_4$  and 10 to 12 g of  $\text{K}_2\text{SO}_4$ , place a funnel in the neck of the flask.

and heat until the solution becomes colorless. Cool, wash the funnel, dilute the solution to 100 ml. with water, and transfer to a 400-ml. beaker. Dilute to 250 ml. with hot water, and precipitate the antimony with  $\text{H}_2\text{S}$ . Filter, and transfer the precipitate to a Kjeldahl flask. Add 15 ml. of  $\text{H}_2\text{SO}_4$  and 10 to 12 g. of  $\text{K}_2\text{SO}_4$ , and heat as described above until the solution is colorless. Wash the funnel, dilute the solution to 100 ml. with water, add 1 to 2 g. of  $\text{Na}_2\text{SO}_3$ , and boil until all the  $\text{SO}_2$  is driven out. This is shown when no blue color is obtained with starch iodate paper. Add 25 ml. of  $\text{HCl}$ , dilute to 200 ml., regulate the temperature to about  $60^\circ\text{C}$ ., add 2 drops of 0.2% methyl red solution, and titrate with 0.1 *N*  $\text{KBrO}_3$  solution until the solution is colorless. When the indicator starts to fade, add the  $\text{KBrO}_3$  slowly, using another drop of indicator if desired. At the end point, an added drop of indicator should become colorless. If iron is found to be absent, it is not necessary to precipitate the antimony with  $\text{H}_2\text{S}$  and the second heating in the Kjeldahl flask may be eliminated.

Calculation.—Calculate the percentage of antimony as  $\text{Sb}_2\text{S}_3$ , as follows:

$$\text{Antimony as } \text{Sb}_2\text{S}_3, \text{ per cent} = \frac{\text{ml. KBrO}_3 \times \text{normality of KBrO}_3 \times 0.0849}{\text{wt. of specimen}} \times 100$$

#### TITANIUM DIOXIDE

*Scope.*—This procedure may be used for determination of  $\text{TiO}_2$  in any rubber product. It may also be used qualitatively to detect the presence of  $\text{TiO}_2$  in the ash of a rubber product. The method is based on fusion of the rubber product ash with potassium pyrosulfate, dissolution of the fused mixture in dilute  $\text{H}_2\text{SO}_4$  and the formation of a colored titanium complex with hydrogen peroxide.

*Calibration of Photoelectric Photometer.*—Accurately weigh 0.125 g. of titanium dioxide into a 30-ml. platinum crucible. Add 6 g. of fused potassium pyrosulfate powder and 2 to 3 drops of  $\text{H}_2\text{SO}_4$ . Heat the crucible gently until all the pyrosulfate is melted. Gradually increase the heat until the bottom of the crucible is a dull red and continue heating until the  $\text{TiO}_2$  is completely dissolved. Allow to cool while carefully rolling the melt around the walls of the crucible to facilitate solution of the fused material. Place crucible and contents in a 150-ml. beaker containing 50 ml. of water. Carefully add, with stirring, 25 ml. of  $\text{H}_2\text{SO}_4$ . Cover the beaker and boil gently until dissolution is complete. Remove the heat and remove crucible from beaker with a glass rod, washing with  $\text{H}_2\text{SO}_4$  (6:100). Cool the solution and transfer to a 250-ml. volumetric flask, rinsing with  $\text{H}_2\text{SO}_4$  (6:100). Dilute to volume with water and mix well. Carry a blank through the same procedure. If a spectrophotometer with 1-cm. cells is used for absorbance measurement, proceed as in (1). If a filter photometer is used for this measurement, proceed as in (2).

(1) Transfer a 15-ml. aliquot of the titanium sulfate solution to a 50-ml. volumetric flask, add 2 ml. of  $\text{H}_3\text{PO}_4$  and 5 ml. of hydrogen peroxide (3%) to the flask and dilute to volume with  $\text{H}_2\text{SO}_4$  (6:100). Allow to stand 5 minutes and measure the absorbance in 1-cm. cells at 416  $\text{m}\mu$ , using  $\text{H}_2\text{SO}_4$  (6:100) in the reference cell. Dilute the blank and measure its absorbance in the same manner. Calculate the absorptivity of  $\text{TiO}_2$  as follows:

$$\text{TiO}_2 \text{ absorptivity, } a = \frac{(A_A - A_B) \times 50}{CD}$$

where  $A_A$  = absorbance of the diluted aliquot containing titanium,

$A_B$  = absorbance of diluted blank aliquot,

$C$  = volume of aliquot taken, ml, and

$D$  = mg of  $TiO_2$  per ml of original solution

NOTE—The nomenclature and abbreviations used are in accordance with ASTM Designation E131 61 T

(2) Obtain data for a calibration curve by diluting aliquots of the  $TiO_2$  solution and of the blank to 50 ml with  $H_2SO_4$  (6 100), after the addition of 2 ml of  $H_3PO_4$  and 5 ml of hydrogen peroxide (3%), and measuring the absorbance against  $H_2SO_4$  (6 100) in a filter photometer using a filter having a maximum transmittance at or near 416  $m\mu$ . From these data construct a calibration curve of mg of  $TiO_2$  per ml of solution against absorbance of the solution minus absorbance of the blank diluted in the same manner. Use only absorbance values between 0.15 and 1.5.

**Procedure**—Accurately weigh a 50 to 60 mg specimen of rubber product into a 3 to 4 ml platinum crucible. If the approximate  $TiO_2$  content is known, adjust specimen size to assure an absorbance reading between 0.15 and 1.5. Place crucible and specimen in a cold muffle furnace and heat to 550°C, continuing heating until no carbonaceous material remains. Remove crucible from furnace, cool, add 15 to 20 g of fused potassium pyrosulfate powder and 2 to 3 drops of  $H_2SO_4$  to the weighed specimen and to a blank crucible. Heat gently until the pyrosulfate is melted. Gradually increase heat until the bottom of the crucible is dull red and continue heating for 10 to 15 minutes. Any residue at this point is silica or clay. Cool crucible while carefully rolling the melt around the inside of the crucible. Place crucible and contents in a 50 ml beaker, cover with  $H_2SO_4$  (6 100), cover the beaker with a watch glass and boil the mixture slowly until dissolution is complete except for clay or silica. Remove the heat and remove the crucible from the beaker with a glass rod, washing with  $H_2SO_4$  (6 100). Filter through paper or a filter crucible if solution is not perfectly clear and quantitatively transfer solution to a 50 ml volumetric flask using  $H_2SO_4$  (6 100) for rinsing beaker and filter. Add 2 ml  $H_3PO_4$  and 5 ml hydrogen peroxide (3%) to the flask and dilute to volume with  $H_2SO_4$  (6 100). Mix and allow flask to stand for 5 minutes. Measure the absorbance of the unknown solution and the blank at 416  $m\mu$  using  $H_2SO_4$  (6 100) in the reference cell of the spectrophotometer or filter photometer. If the absorbance is greater than 1.500, add 2 ml of hydrogen peroxide (3%) to an aliquot of the solution and dilute to a known volume with  $H_2SO_4$  (6 100). Measure absorbance at 416  $m\mu$ . If the absorbance is less than 0.150 a larger specimen shall be used for the determination.

**Calculations.**—Calculate the percentage of  $TiO_2$  in the specimen as in (1) if a spectrophotometer was used for measuring absorbance and as in (2) if a filter photometer was used for absorbance measurements

$$(1) \quad \text{Titanium dioxide, per cent} = \frac{(A_S - A_B) \times 100}{aE},$$

where  $A_S$  = absorbance of specimen solution,

$A_B$  = absorbance of blank solution,

$a$  = absorptivity of  $TiO_2$ , and

$E$  = mg. of specimen per ml of solution on which  $A_S$  is measured

(2) Calculate  $A_S$  minus  $A_B$ . From the calibration curve determine the mg of  $TiO_2$  per ml of solution

$$\text{Titanium dioxide, per cent} = \frac{\text{mg. of TiO}_2 \text{ per ml. of solution} \times 100}{\text{mg. of specimen per ml. of the same solution}}$$

Reproducibility.—Duplicate results by one operator should check within 0.6%, based on the weight of the specimen.

### FREE CARBON

*Procedure.*—Extract a 0.5-g. specimen with acetone-chloroform mixture according to Total Extract Method, page 2205.

Transfer the specimen to a 250-ml. beaker and heat on the steam bath until it no longer smells of chloroform. Add a few ml. of  $\text{HNO}_3$  and allow to stand for about 10 minutes. Add 50 ml. more of  $\text{HNO}_3$ , taking care to wash down the sides of the beaker, and heat on the steam bath for at least 1 hour. At the end of this time there should be no more bubbles or foam on the surface. Pour the liquid, while hot, into a Gooch crucible, taking care to keep as much as possible of the insoluble material in the beaker. Filter slowly with gentle suction and wash well by decantation with hot  $\text{HNO}_3$ . (*Caution.*—Empty the filter flask.) Wash with acetone and a mixture of equal parts of acetone and chloroform until the filtrate is colorless. Digest the insoluble material, which has been carefully retained in the beaker, for 30 minutes on the steam bath with 35 ml. of  $\text{NaOH}$  solution (300 g. per l.). This treatment with alkali may be omitted if silicates are absent. Dilute to 60 ml. with hot water and heat on the steam bath. Filter the solution of alkali and wash well with hot  $\text{NaOH}$  solution (175 g. per l.).

*NOTE.*—The filtration may be materially aided, particularly with some synthetic rubber products, by partial or complete neutralization of the  $\text{HNO}_3$  solution with  $\text{NH}_4\text{OH}$ . Partial neutralization together with the addition of trivalent cations or anions may also aid agglomeration of the carbon black particles if they are too well dispersed to filter.

Wash the residue about four times with hot  $\text{HCl}$ . Neutralize the last washing with  $\text{NH}_4\text{OH}$  and test for the presence of lead with  $\text{Na}_2\text{CrO}_4$  solution. If lead is present, continue to wash with hot  $\text{HCl}$  and, finally, wash with warm  $\text{HCl}$  (1:7). Remove the crucible from the funnel, taking care that the outside is perfectly clean, dry it in an air bath for  $1\frac{1}{2}$  hours at  $110^\circ\text{C}.$ , cool, and weigh; call this weight *a*. Burn off the carbon at a dull red heat and reweigh; call this weight *b*. The difference in weight represents approximately 105% of the carbon originally present in the form of lampblack or gas black.

*Calculation.*—Calculate the percentage of free carbon as follows:

$$\text{Free carbon, per cent} = \frac{a - b}{1.05 \times \text{wt. of sample}} \times 100$$

### GLUE DETERMINATION

The glue content may be determined on an acetone extracted sample by the procedure given for Protein Content, page 2163, using a factor of 6.5 for converting the per cent nitrogen to per cent glue. This figure is then substituted in the formula for calculating rubber hydrocarbon when natural rubber is involved and the rubber, as compounded, is calculated from this value. The corrected glue content is calculated as follows:

Glue, corrected, per cent = total nitrogen as glue, per cent

$$- (\text{rubber as compounded} \times 0.004 \times 6.5)$$

NOTE—This calculation assumes that the rubber as compounded contains 0.4% protein nitrogen

### CELLULOSE DETERMINATION (ASTM Designation D297-59T)

**Procedure**—Extract a 0.5 g specimen with acetone-chloroform mixture and place in a 250 ml lipped assay flask with 25 ml of rubber solvent oil. Place in an oil bath at 150 to 165°C until small particles can be seen distinctly in the supernatant liquid which requires about 3 hours. Dilute with 15 ml of benzene and 200 ml of petroleum ether. Filter through a Gooch crucible and wash the residue thoroughly with warm acetone. Treat repeatedly with hot HCl (1:3) until the residue is free of acid soluble fillers. Wash the pad well with boiling water and run small portions of acetone through it until the filtrate is colorless. Wash with alcohol and dry at 105°C to constant weight. Remove the pad from the crucible with the help of a pair of sharp pointed tweezers using the under portion of the pad as a swab to clean the sides of the crucible and place all of this material in a tared weighing bottle. Replace in the drying oven for about 10 minutes, cool and weigh. Weight of weighing bottle, pad, insoluble fillers and cellulose minus weight of the weighing bottle equals weight of pad, insoluble fillers and cellulose.

Transfer the contents of the weighing bottle to a 50 ml beaker and pour over it 15 ml of acetic anhydride and 0.5 ml of H<sub>2</sub>SO<sub>4</sub>. Digest the mixture on a steam bath for 1 hour. (The time and temperature of the digestion are important.) After the mixture has cooled thoroughly dilute with 25 ml of acetic acid (90%) and filter through a weighed Gooch crucible. To guard against traces of the material being carried through this filtration as well as the ones to follow shall be very slow and only gentle suction shall be used. Wash with hot acetic acid (90%) until the filtrate comes through absolutely colorless and then wash about four times more. Wash with acetone about five times. After having taken care that all of the material has been washed out of the beaker in which the acetylation took place remove the crucible from the funnel, clean the outside thoroughly and dry for 2 hours at 150°C. Cool and weigh. The original weight of the crucible plus weight of pad, fillers and cellulose minus the weight of the crucible after acetylation equals cellulose.

**Calculation**—Calculate the percentage of cellulose as follows

$$\text{Cellulose per cent} = \frac{\text{cellulose}}{\text{wt of specimen}} \times 100$$

NOTE—This method is very poor at best but is the only method available at this time. The results obtained by this procedure should be very carefully evaluated in terms of the operator's experience.

### IDENTIFICATION OF ACCELERATORS AND ANTIOXIDANTS

It should be made clear at the outset of this section that there is no standard method for the identification of the chemicals used in rubber compounds for the acceleration of the vulcanization process or for the agents used in rubber to protect against thermal or oxidative degradation. It is quite probable that there will never be a generally useful method that does not require revision at least once a year because of the constantly changing group of chemicals used as vulcanization accelerators and as antioxidants. It should also be made clear that it is seldom possible to actually identify the accelerators used in a vulcanized rubber compound as specific individual compounds because the acceleration mechanism usually changes the

chemical composition of the accelerators. To illustrate this point, it is usually not possible to tell whether a thiuram disulfide or a dithiocarbamate was originally present because the residues remaining after cure are either dithiocarbamates or the amines formed by decomposition. 2-Mercaptobenzothiazole can be detected readily in a rubber compound, but it would be very difficult to determine whether it was originally added as such or as one of the many derivatives of this compound currently in use. However, it is still possible to obtain an idea of the type of curing system used and to identify many of the fragments remaining after vulcanization. The antioxidants and the antiozonants can also be separated from a rubber compound and be identified or at least classified as to type. Again, the influx of new commercial products makes this task more difficult, particularly since many of the materials used are complex mixtures and many of them differ only slightly from each other in composition or in chemical reactivity. The complexity of the problem has led to a large number of publications on the subject. Some of these are limited to the detection of one or two components in simple rubber compounds or in crude rubber. The ideal techniques for this detection are infrared and ultraviolet spectrophotometry applied to the isolated chemical. There are several papers devoted to the separation of relatively complex mixtures of these chemicals extracted from a rubber compound. The methods make use of the only technique that has any chance of solving this problem, chromatography. Unfortunately, the application of this method has been made more difficult by the use in modern practice of large quantities of oils and softeners in the rubber compounds. These materials often accompany the accelerators and antioxidants during development of the chromatogram and render color spotting more difficult.

For these reasons, no single method is given in this chapter as a standard method, but a digest of three of the more promising methods in use today is given, with some remarks on their application.

**1. Accelerator Identification Scheme.**—The paper by Kress and Mees<sup>29</sup> describes an analysis scheme for accelerators only, based on acid and base extractions of the rubber sample followed by selective solvent extraction to isolate the accelerators and accelerator residues. The accelerators are then identified by their ultraviolet absorption spectra. Other tests can also be applied. Softeners do not interfere and some materials can be separated and identified better than with the other methods discussed here. A few of the accelerator fragments cannot be distinguished, but the type of accelerator can be established.

**2. Column Chromatography, Accelerators and Antioxidants.**—While more than one method has been proposed for separation and identification of these materials by column chromatography, the papers by Parker and Berriman<sup>30</sup> appear to have the most merit. Extracts of the rubber are dissolved in methylene chloride and placed on a silica gel/Celite column. Seven sets of developing solvents are used to produce zone separation on the columns. The columns are extruded from the tube and streaked with different reagents in order to produce colors characteristic of the materials present. Both the position on the column and the colors are characteristic of the chemicals. Stearic acid and some processing oils interfere or change the position of the zones on the column. In spite of its disadvantages

<sup>29</sup> K. E. Kress and F. G. S. Mees, *Anal. Chem.*, **27**, 528 (1955).

<sup>30</sup> C. A. Parker and J. M. Berriman, *Rubber Chem. and Technol.*, **26**, 449 (1953); *Ibid.*, **27**, 1013 (1954).



the method is useful both for preliminary work and in many cases for final identification

3. *Paper Chromatography, Accelerators and Antioxidants.*—Paper chromatography is probably the most rapid method, and it is most likely to give separation of the largest number of materials. Zijp<sup>21</sup> has covered this method quite thoroughly in his papers. The rubber extract is divided into several portions and each portion is evaporated. HCl,  $\text{NH}_4\text{OH}$ , and ethanol extracts are obtained from the original acetone extract and small portions of these are spotted on nine different papers, some of which are plain paper and others acetylated cellulose. The chromatograms are developed with a specific mobile phase, the papers are sprayed with suitable reagents, and the color and  $R_f$  values of the resulting color spots are noted. The method can be speeded up, with some loss of resolution, by employing horizontal circular paper in a covered Petri dish. This method is also subject to some of the disadvantages of Method 1 because the acid extract decomposes some accelerator fragments still further. It is rarely possible to detect the original accelerator itself, especially the thiuram disulfides, the dithiocarbamates and the 2-mercapto benzothiazole derivatives. Since this scheme identifies individual primary and secondary amines, there is a compensating advantage in that fragments may be detected when the original compound is completely altered during vulcanization. Thus the method is particularly useful in identifying the various  $N$ -alkyl or  $N$ -dialkyl 2-benzothiazolylsulfenamides which are used as commercial accelerators.

Method 3 is capable of separating most of the common accelerators or their fragments, the amine-type antioxidants and many of the phenolic antioxidants. No provision has been made for some of the  $p$ -phenylenediamine derivatives classed as antioxidants but it should be possible to fit them into the scheme. Processing oils tend to interfere in some cases by spreading the spots on the paper or by masking colors. Wake<sup>22</sup> also describes this method in some detail as well as the column chromatography method.

Thus it appears possible to use one or more of these methods to obtain a quite complete analysis of the curing and antioxidant system in any rubber compound. It is obvious, however, that a great deal of work will be necessary before any of these methods can be considered as standard methods.

<sup>21</sup> J. W. H. Zijp, *Rubber Chem. and Technol.*, **30**, 705 (1957).

## Chapter 44

# SILICATES: GLASSES, ROCKS, AND FERROUS SLAGS

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Procedures for the analysis of all silicates would include methods for most of the known elements. Obviously, space will not permit an attempt to give such procedures here. The procedures given have been selected as representative and should satisfy the majority of commercial silicate analysis needs. Methods for the less important and less widely encountered elements are not given. The applicability of these procedures to a given sample without modification will usually depend upon the elements present other than those indicated. An attempt has been made to list interfering elements which are likely to occur in the samples under consideration. In general, a good qualitative analysis is very valuable when decisions must be made concerning the applicability of a particular procedure to a sample similar to those chosen here.

## SAMPLING

Most commercially available glasses are relatively homogeneous and sampling them presents no particular problem. Usually, a good-sized piece of the glass to be analyzed is crushed (provide protection for the eyes from any flying chips) and ground in an agate mortar.

Proper sampling of the heterogeneous materials for which analysis procedures are given for the analysis of Silicate Rocks and Ferrous Slags is a more complicated task. Directions for the sampling of solid materials are given in another chapter of this book and will not be repeated here. It will be assumed that the sample referred to in the following procedures is representative of the bulk material from which it was taken.

The sample should be ground to a suitable particle size before it is treated as directed in the procedures. The phrase "ground sample" is used here to designate

a sample which has been ground to pass through a 100 mesh sieve. Where less grinding is needed, the sieve mesh through which the sample should pass will be specified. Contamination during the grinding process with minor constituents for which analyses are to be made, such as iron and aluminum, is particularly to be avoided. Steel alumina (Diamonite, sapphire) mullite and porcelain mortars generally should not be used for grinding glasses for this reason. In general, the mortar material should be chosen so that the contamination which occurs during grinding is unimportant. This usually means that the mortar should contaminate the sample only with the major constituents of the sample or with constituents for which analyses will not be made.

# THE ANALYSIS OF GLASSES

For the purposes of this chapter, silicate glasses are grouped into three composition classes, namely: (1) soda-lime glasses, (2) lead glasses, and (3) borate glasses. These three groups will encompass a large majority of the commercially available glasses. The first class includes window or sheet glass, plate glass and most bottle or container glasses. The second class includes fine crystal glasses, some optical glasses, some bottle and bulb glasses and radiation shielding glasses. The third class includes most fiber glasses and chemical-resistant glass. It will be obvious to those familiar with glass compositions that these three classes overlap, and that they contain glasses other than those listed.

## THE ANALYSIS OF SODA-LIME GLASSES

The following procedures are applicable to silicate glasses containing sodium, potassium, calcium and/or magnesium as major constituents. In general, they are applicable to such glasses containing up to 3%  $\text{Al}_2\text{O}_3$ , 2%  $\text{BaO}$ , 1%  $\text{SO}_3$ , 1%  $\text{Fe}_2\text{O}_3$ , 0.5%  $\text{Cl}$ , 0.25%  $\text{As}_2\text{O}_3$ , 0.25%  $\text{Sb}_2\text{O}_3$ , 0.2%  $\text{MnO}$ , 0.1%  $\text{ZrO}_2$ , 0.1%  $\text{TiO}_2$ , 0.1%  $\text{ZnO}$  and 0.05%  $\text{PbO}$ .

Complete analyses such as may be obtained with the Regular Procedures (pages 2229–2235) often are not needed. In such instances, a more rapid partial analysis for selected constituents usually is desired. The Rapid Procedures (pages 2235–2242) are designed to meet this need. The analyses for Coloring Elements are separated into a separate section because these are usually determined on separate samples, and also because they are often the only elements for which analyses are made on a given sample.

## REGULAR PROCEDURES

**Reagents Required.**—Unless a specific concentration is mentioned here, the usual concentrated, reagent-grade materials are meant. Examples are: 28%  $\text{NH}_4\text{OH}$ , 38%  $\text{HCl}$ , 48%  $\text{HF}$ , 70%  $\text{HNO}_3$ , 70%  $\text{HClO}_4$ , 85%  $\text{H}_3\text{PO}_4$ ,  $\text{H}_2\text{SO}_4$ —sp. gr. 1.84. Also, sources have been listed for some of the more uncommon materials. Special reagents will be listed with each determination.

### DETERMINATION OF SILICON ( $\text{SiO}_2$ )

**Procedure.**—Accurately weigh a 1-g. ground sample into a platinum dish. Add about 3 g. of sodium carbonate and mix with a small spatula. Push the mixture to the center of the dish and cover as evenly as possible with an additional gram of sodium carbonate. Cover the dish with a platinum lid and heat slowly over a Meker burner, gradually increasing the heat until a clear fusion is obtained. Maintain this temperature for 10 minutes. Cool with the dish covered to avoid loss.

Add 30 ml. of 1:1  $\text{HCl}$  and heat on a steam bath with the cover slightly displaced until disintegration is complete. Wash the cover with hot water and remove it. Evaporate to dryness on a steam bath. Heat on a hot plate (60–70°C.) until the odor of  $\text{HCl}$  can no longer be detected (about 1 hour). Add 20 ml. of 1:3

HCl, heat for 10 minutes and filter onto a coarse filter paper (e.g., B&A grade 0) into a glazed porcelain casserole. Scrub the platinum dish and wash the residue with hot water until the wash water gives only a faint opalescence with silver nitrate solution. Place the filter paper and precipitate in an unweighed platinum crucible.

Evaporate the filtrate to dryness. Continue heating until the odor of HCl can no longer be detected. Add 10 ml of 1:3 HCl, heat for 5–10 minutes to dissolve the soluble salts and filter into a 250 ml beaker. Scrub the casserole and wash the precipitate with hot water until free of chlorides. Save the filtrate for the sulfate determination. Place the filter paper and precipitate in the platinum crucible containing the first precipitate. Char the filter paper slowly. When the precipitate is white, place the crucible in a muffle furnace and ignite to a constant weight at 1000–1050°C. Cool in a desiccator and weigh. Moisten the  $\text{SiO}_2$  with water, add 6 drops of 1:1  $\text{H}_2\text{SO}_4$  and 10 ml 48% HF. Evaporate to dryness and reignite for 5 minutes at 1000°C. Cool in a desiccator and weigh. The loss in weight is  $\text{SiO}_2$ .

$$\text{Per cent SiO}_2 = \frac{\text{Wt SiO}_2 \times 100}{\text{Wt sample}}$$

#### DETERMINATION OF SULFUR (TOTAL $\text{SO}_3$ )

**Procedure**—Add 5 ml of bromine water to the filtrate from the  $\text{SiO}_2$  determination. Boil rapidly until the bromine is volatilized. Add several drops of methyl red indicator (0.1% alcoholic solution). Neutralize to the yellow color of the indicator with  $\text{NH}_4\text{OH}$ , reacidify with concentrated HCl, and add 6–10 drops of HCl in excess. Heat to boiling, add dropwise 5 ml of 10% barium chloride solution and boil for 10 minutes. The final volume should be approximately 100 ml. Let stand in a warm place for 2 hours. Filter onto a fine filter paper (e.g., Whatman No. 42) containing a small amount of filter pulp. Wash with water until a test for chlorides gives only a faint opalescence.

Place the precipitate in a weighed platinum crucible and ignite carefully without inflaming the paper. Cool and add a drop of 1:1  $\text{H}_2\text{SO}_4$  and a few drops of 48% HF. Evaporate carefully to dryness and ignite to constant weight in a muffle furnace at 900°C. Cool in a desiccator and weigh the residue as  $\text{BaSO}_4$ .

$$\text{Per cent SO}_3 = \frac{\text{Wt BaSO}_4 \times 0.3430 \times 100}{\text{Wt sample}}$$

#### DETERMINATION OF BARIUM ( $\text{BaO}$ )

**Procedure**—Accurately weigh a 1 g ground sample into a platinum dish. Add 15 ml of HF and 5 ml of  $\text{HNO}_3$ . Cover and evaporate to dryness. Add 5 ml of 1:1  $\text{H}_2\text{SO}_4$ , warm until fumes of sulfuric acid appear. (In laboratories equipped to use perchloric acid, treat the glass sample with several ml of water, 5 ml of  $\text{HClO}_4$ , 15 ml of HF, cover and evaporate to fumes of perchloric acid. Remove the lid, rinse the lid and sides of the dish with water and evaporate to dryness.) To the residue in the dish add 2 ml of concentrated HCl and 20 ml of water and warm to dissolve the soluble salts. Cool and scrub the lid and dish with a rubber policeman and transfer the contents to a 250 ml beaker. Place a small piece of filter paper under a glass rod in the beaker to prevent bumping. Add 100 ml of

water and heat to boiling. (If the  $\text{HClO}_4$  procedure was used, add 4 ml. of 1:1  $\text{H}_2\text{SO}_4$ .) Boil for 10 minutes and let stand in a warm place for 2 hours.

Filter onto a fine filter paper, containing a small quantity of paper pulp, into a 250-ml. beaker. Wash thoroughly with warm water. Save the filtrate for the determination of  $\text{As}_2\text{O}_5$ . Transfer the paper and precipitate to a weighed platinum crucible and ignite without inflaming. Add 1 drop of 1:1  $\text{H}_2\text{SO}_4$  and 1 ml. of HF to the ignited precipitate. Evaporate to dryness at a very low heat. Ignite in a muffle furnace at  $900^\circ\text{C}$ . for 15 minutes. Cool in a desiccator and weigh the residue as  $\text{BaSO}_4$ .

$$\text{Per cent BaO} = \frac{\text{Wt. BaSO}_4 \times 0.6570 \times 100}{\text{Wt. sample}}.$$

#### DETERMINATION OF ARSENIC ( $\text{As}_2\text{O}_5$ )

**Reagents.** 0.1 N Iodine Standard Solution.—Weigh 12.7 g. of pure iodine into a small beaker, add 40 g. of KI (free from iodate) and cover with distilled water. Stir occasionally and let stand until dissolved. Filter through a medium-porosity glass filtering crucible into a 1-liter volumetric flask. Dilute to volume and store in an amber bottle.

Standardize the iodine solution against primary standard  $\text{As}_2\text{O}_3$  as follows: Weigh accurately 0.20 g. of dry  $\text{As}_2\text{O}_3$  into a 250-ml. Erlenmeyer flask. Dissolve in 10 ml. of 1 N NaOH and add cautiously 15 ml. of 1 N  $\text{H}_2\text{SO}_4$ . Dilute to 100 ml. with water and add slowly 5 g. of sodium bicarbonate and 5 ml. of starch indicator. Then titrate with the iodine solution to the first permanent blue color. Determine a blank on the reagents plus 2.0–2.5 g. of KI in a 100-ml. volume and deduct this volume from the total iodine consumed.

$$N_{\text{I}_2} = \frac{\text{Wt. As}_2\text{O}_3 \times 20.22}{\text{ml. I}_2}.$$

$$\text{As}_2\text{O}_5 \text{ titer} = N_{\text{I}_2} \times 0.05746.$$

$$\text{Sb}_2\text{O}_5 \text{ titer} = N_{\text{I}_2} \times 0.08088.$$

**Starch Indicator.**—Weigh 2.5 g. of soluble starch into a beaker and mix with 25 ml. of cold water. Add 500 ml. of boiling water, boil for 10–15 minutes, cool and add 2 ml. of chloroform or a crystal of thymol.

**Procedure.**—Evaporate the filtrate from the barium separation to dryness, add 70 ml. of water and 30 ml. of concentrated HCl and warm to dissolve the residue. Pass in  $\text{H}_2\text{S}$  at 0 to  $10^\circ\text{C}$ . for 30 minutes to precipitate the arsenic. Let stand at this temperature for 2 hrs. Filter through a coarse filter paper (e.g., Whatman No. 40) containing a small amount of paper pulp and wash with a 30% HCl solution saturated with  $\text{H}_2\text{S}$ . Save the filtrate for the determination of antimony. Dissolve the arsenic precipitate with 2–3 ml. of concentrated  $\text{NH}_4\text{OH}$  into a 250-ml. beaker and wash the paper thoroughly with hot water. To this solution, add 5 ml. of 3%  $\text{H}_2\text{O}_2$ , cover the beaker and boil. Evaporate slowly on a hot plate to a volume of 15 ml., cool, add 7 ml. of 1:1  $\text{H}_2\text{SO}_4$  and boil for 15 minutes. Transfer the solution to a 300-ml. Erlenmeyer flask which has been marked at levels corresponding to 40 and 100 ml. Dilute the solution to 100 ml. with hot water. Add 0.3 g. of KI, boil vigorously and pass a stream of  $\text{CO}_2$  through the hot solution. When the volume is reduced to 40 ml., add 25 ml. of hot water, another fragment

of KI and evaporate again to 40 ml. Repeat this operation until the solution becomes colorless. Dilute at once to 100 ml with cold water and cool quickly to slightly below 20°C. Neutralize most of the  $H_2SO_4$  by adding carefully 12 to 14 ml of a saturated potassium or sodium carbonate solution. Complete the neutralization by adding solid sodium bicarbonate until red litmus in the solution turns blue then add 2 g in excess. The temperature of the solution should be 20–25°C. Add 5 ml of starch indicator and titrate the arsenic with 0.1 N iodine solution to the appearance of a blue color.

$$\text{Per cent } As_2O_5 = \frac{\text{Ml iodine} \times As_2O_5 \text{ titer} \times 100}{\text{Wt sample}}$$

#### DETERMINATION OF ANTIMONY ( $Sb_2O_5$ )

*Reagents* See Determination of Arsenic

*Procedure*—Dilute the filtrate from the arsenic precipitation with water to make the solution approximately 20% HCl by volume. Heat to 80–90°C and pass in a rapid stream of  $H_2S$  until the solution is clear and the precipitate is black. Let stand overnight, filter the precipitate onto a coarse filter paper and wash with a 5% HCl solution saturated with  $H_2S$ . Save the filtrate for the  $R_2O_3$  determination.

Place the paper containing the antimony sulfide in a 150 ml beaker and add 10 ml of water, 10 ml of HCl and 5 g of tartaric acid. Macerate the paper and heat gently until the precipitate is dissolved. Filter onto a coarse filter paper into a 300 ml Erlenmeyer flask and wash with warm water. Boil the filtrate until hydrogen sulfide is no longer evolved. Adjust the pH as follows: (1) with a 10% solution of sodium hydroxide (red litmus turns blue), (2) with HCl until just acid and (3) add solid sodium bicarbonate until approximately a 2 g excess remains undissolved. Add 5 ml of starch indicator and titrate immediately with 0.1 N iodine solution to the appearance of a blue color.

$$\text{Per cent } Sb_2O_5 = \frac{\text{Ml iodine} \times Sb_2O_5 \text{ titer} \times 100}{\text{Wt sample}}$$

#### DETERMINATION OF TOTAL $R_2O_3$ ( $Fe_2O_3$ , $Al_2O_3$ , $TiO_2$ , $MnO$ )

*Procedure*—To the filtrate from the antimony separation add 10 ml of bromine water and boil to expel the  $H_2S$  and the excess bromine. Add several drops of 0.1% alcoholic methyl red indicator. Add  $NH_4OH$  dropwise until the solution becomes a distinct yellow then add 6–10 drops in excess. Boil for 1–2 minutes. Cool slightly and filter through a coarse filter paper that contains a small quantity of filter pulp. Dissolve the precipitate from the filter paper with 20 ml of hot 1:1 HCl into the precipitation beaker. Wash the paper with hot water. Dilute the solution to a volume of 50 ml and reprecipitate the  $R_2O_3$  group as before. Filter through a coarse filter paper into a 250 ml beaker and wash with a hot 2% ammonium nitrate solution until silver nitrate gives only a faint opalescence in the filtrate. If desired this filtrate can be used for the determination of calcium beginning with the fourth paragraph of the Regular Procedure for Calcium. Place the paper and precipitate in a weighed platinum crucible. Ignite gently until the carbon has been removed then ignite to a constant weight in a muffle furnace at 1000°C. Cool in a desiccator and weigh as total  $R_2O_3$ .

$$\text{Per cent } R_2O_3 = \frac{\text{Wt } R_2O_3 \times 100}{\text{Wt sample}}$$

## DETERMINATION OF CALCIUM (CaO)

**Reagent.** Potassium Permanganate Standard Solution, 0.1 *N*.—Weigh accurately 3.16 g. of reagent grade  $\text{KMnO}_4$ . Dissolve in one liter of distilled water and boil for five minutes. Let the solution cool. Filter through a fritted glass filtering crucible and store in an amber bottle.

Standardize the permanganate against primary standard sodium oxalate as follows: Weigh 0.200 g. of dried sodium oxalate into a 400-ml. beaker. Add 100 ml. of  $\text{CO}_2$ -free hot (80–90°C.) water and 5 ml. of 1:1  $\text{H}_2\text{SO}_4$ . Titrate at once with the permanganate solution to the first pink tint that persists for 60 seconds. The temperature of the solution should not be below 60°C. Determine a blank on the water and acid, and subtract this value from the volume of permanganate required for the titration.

$$N_{\text{KMnO}_4} = \frac{\text{Wt. Na}_2\text{C}_2\text{O}_4 \times 14.92}{\text{Ml. KMnO}_4}$$

$$\text{CaO titer} = N_{\text{KMnO}_4} \times 0.02804$$

**Procedure.**—Accurately weigh a 0.5-g. ground sample into a platinum dish. Add 5 ml. of  $\text{HNO}_3$ , 15 ml. of  $\text{HF}$  and evaporate to dryness. Place a platinum cover on the dish, moisten the residue with 2 ml. of 1:1  $\text{H}_2\text{SO}_4$  and heat until fumes of  $\text{H}_2\text{SO}_4$  appear. Remove the cover and expel the remaining  $\text{H}_2\text{SO}_4$  at the lowest possible temperature. Cool, wash the lid with hot water and add 20 ml. of 1:3  $\text{HCl}$ . Heat gently, stirring with a glass rod, until the soluble residue is in solution. (If barium is present, it will form insoluble  $\text{BaSO}_4$  which can be removed by filtering onto a fine filter paper and washing with water.) Transfer the solution to a 150-ml. beaker with a final volume of about 60 ml.

When arsenic and antimony are present in the sample, transfer the solution to a 250-ml. beaker, add 15 ml. of  $\text{HCl}$ , dilute to about 100 ml. and treat with  $\text{H}_2\text{S}$  gas for 20 minutes. Let stand overnight, filter through a coarse filter paper and wash several times with a 10%  $\text{HCl}$  solution saturated with  $\text{H}_2\text{S}$ . Discard the precipitate and boil the filtrate to expel the hydrogen sulfide.

Add 5 ml. of bromine water and boil to volatilize the bromine. Add several drops of methyl red indicator. Place a small piece of filter paper under the end of a glass rod in the beaker to prevent bumping. Add  $\text{NH}_4\text{OH}$  dropwise until the indicator turns to yellow, then add 4–5 drops in excess. Boil for about one minute to coagulate the precipitate. Add a small amount of paper pulp to the beaker, cool slightly and filter through a coarse filter paper into a 250-ml. beaker. Wash the  $\text{R}_2\text{O}_3$  precipitate with hot 2% ammonium chloride solution until the filtrate has reached a volume of 120 ml. Discard the precipitate.

Add 1:1  $\text{HCl}$  to the filtrate to obtain the red color of methyl red indicator, heat to boiling (prevent bumping) and add 10 ml. of a saturated ammonium oxalate solution. Precipitate the calcium by adding  $\text{NH}_4\text{OH}$  dropwise until a peach color of the methyl red indicator is obtained. Boil 5–10 minutes, add 6–10 drops of  $\text{NH}_4\text{OH}$  and keep warm for 30 minutes. Cool and decant the solution through a fine filter paper into a 400-ml. beaker. (Start evaporating this first filtrate for the magnesium determination.) Place the precipitation beaker under the funnel and puncture the filter paper with a pointed glass rod. Dissolve the precipitate by washing 10 times with 4 ml. portions of hot 1:3  $\text{HCl}$ , followed by the same amount of washing with hot water. Discard the filter paper. Reprecipitate the calcium as directed previously after adding 5 ml. of a saturated ammonium oxalate solu-



tion Filter through a fine filter paper into the 400 ml beaker that contains the solution for the determination of MgO Wash the precipitate by decanting 4 or 5 times with water that contains 5 drops of  $\text{NH}_4\text{OH}$  per 500 ml Wash the filter paper 5 times Drain the stem of the filter funnel into the filtrate Wash the precipitate back into the precipitation beaker with hot water Save the filter paper Add 10 ml of 1:1  $\text{H}_2\text{SO}_4$  to the beaker to dissolve the  $\text{CaC}_2\text{O}_4$  dilute to about 75 ml and heat to boiling Titrate the hot solution with 0.1 N  $\text{KMnO}_4$  to the appearance of the first pink color that persists for one minute Place the filter paper in the beaker Warm the solution and again titrate to a pink color that persists for one minute

$$\text{Per cent CaO} = \frac{\text{Ml KMnO}_4 \times \text{CaO titer} \times 100}{\text{Wt sample}}$$

#### DETERMINATION OF MAGNESIUM (MgO)

**Reagent** 8-Hydroxyquinoline 5%—Dissolve 5 g of finely powdered 8-hydroxyquinoline in 12 ml of glacial acetic acid and 75 ml of water warm to 60°C and stir until solution is complete Filter into an amber bottle and dilute to 100 ml with water

**Procedure**—Evaporate the combined filtrates from the calcium determination to a volume of 150 ml Add several drops of 0.1% alcoholic methyl red indicator Add  $\text{NH}_4\text{OH}$  until the solution becomes a distinct yellow then add 5 ml in excess Add 4 ml of (5%) 8-hydroxyquinoline solution Heat to 60–70°C stir and continue heating 10–15 minutes Do not boil

Let stand 4–6 hours (overnight if convenient) and filter on a medium porosity porcelain filter crucible Save the filtrate for the determination of the total alkalies Wash about 10 times with hot 1:40  $\text{NH}_4\text{OH}$  and dry in an oven at 110°C for 2 hours Cool in a desiccator and weigh as  $\text{Mg}(\text{C}_9\text{H}_6\text{NO})_2 \cdot 2\text{H}_2\text{O}$

$$\text{Per cent MgO} = \frac{\text{Wt Mg}(\text{C}_9\text{H}_6\text{NO})_2 \cdot 2\text{H}_2\text{O} \times 0.1155 \times 100}{\text{Wt sample}}$$

#### DETERMINATION OF TOTAL ALKALIES ( $\text{Na}_2\text{O} + \text{K}_2\text{O}$ )

**Procedure**—Evaporate the filtrate from the MgO determination to about 100 ml in a glazed porcelain casserole Cover with an inverted funnel which will fit just inside the casserole Destroy the ammonium salts with  $\text{HNO}_3$  as follows

Add 20 ml  $\text{HNO}_3$  heat gently for about 20 minutes cool the solution add another 20 ml portion of  $\text{HNO}_3$  and boil the solution gently to dryness Increase the heat slightly to decompose the ammonium salts

Rinse the funnel into the casserole with a little hot water Evaporate the solution to 5–10 ml Add 3 drops of methyl red indicator and 1–2 drops of the (5%) 8-hydroxyquinoline solution Make the solution just alkaline with 1:1  $\text{NH}_4\text{OH}$  and filter through a coarse filter paper into an unweighed 50 ml platinum dish that contains 1 drop of 1:1  $\text{H}_2\text{SO}_4$  Place the platinum dish on a steam bath and evaporate the filtrate to dryness Cover the dish with a platinum lid Heat gently to expel moisture and  $\text{H}_2\text{SO}_4$  Ignite at dull redness (600°C) until the residue is white Cool and add 1 g of ammonium carbonate Heat at dull redness until the ammonium carbonate is volatilized and any carbon is destroyed Cool in a desiccator and weigh

Dissolve the contents of the dish with a few ml of hot water and filter through

a coarse filter paper. The filtrate contains the total alkali sulfates. Wash the filter paper with hot water. Char and ignite the paper in the covered dish at dull redness until the carbon is destroyed. Cool in a desiccator and weigh. The loss in weight is the weight of the combined alkali sulfates.

$$\text{Per cent (Na}_2\text{O} + \text{K}_2\text{O)} = \frac{\text{Wt. alkali sulfates} \times 100}{\text{Wt. sample}}$$

#### DETERMINATION OF CHLORIDE (Cl) <sup>1</sup>

**Procedure.**—Accurately weigh a 5-g. ground sample into a platinum dish. Add 0.1 g. of silver sulfate, 5 ml. of water, 50 ml. of HF and 10–15 ml. HClO<sub>4</sub>. Cover and evaporate to incipient fumes of HClO<sub>4</sub>.

Cool, transfer the solution to a beaker and dilute with 400 ml. of 1:99 HNO<sub>3</sub>. Let stand overnight, filter through a fine filter paper and wash with 100 ml. of cold 1:99 HNO<sub>3</sub>. Immediately dissolve the silver chloride from the paper with warm 5:95 NH<sub>4</sub>OH, dilute to 100 ml. with water and make just acid to litmus paper with 1:1 HNO<sub>3</sub>. Heat the solution to 70–80°C., and add dropwise a slight excess of 1% silver nitrate solution. Heat to boiling and let stand overnight in a dark place. Filter through a weighed filtering crucible containing a glass fiber filter mat, wash the precipitate several times, first with cold 1:99 HNO<sub>3</sub>, then with water. Dry the crucible and precipitate for 1 hour at 130°C., cool in a desiccator and weigh as AgCl.

$$\text{Per cent Cl} = \frac{\text{Wt. AgCl} \times 0.2474 \times 100}{\text{Wt. sample}}$$

### RAPID PROCEDURES

#### DETERMINATION OF SILICON (SiO<sub>2</sub>)

**Reagents.** 1-Amino-2-Naphthol-4-Sulfonic Acid Reductant Solution.—Dissolve separately 10 g. of NaHSO<sub>3</sub> in 50 ml. of water and 0.80 g. of Na<sub>2</sub>SO<sub>3</sub> in 10 ml. of water. Add 0.16 g. of 1-amino-2-naphthol-4-sulfonic acid to the latter and mix the two solutions. Filter through a coarse filter paper into a 100-ml. volumetric flask and dilute to volume. Transfer to a polyethylene bottle and label with the date made. The solution retains its power as a reductant for 7–10 days.

**Ammonium Molybdate.**—Dissolve 7.5 g. of ammonium molybdate (4H<sub>2</sub>O) in water. Add 18 ml. of 1:1 H<sub>2</sub>SO<sub>4</sub> and dilute to 100 ml.

**Silica-Free NH<sub>4</sub>OH (Specific Gravity 0.90).**—Introduce the gas from a cylinder of liquid ammonia through plastic tubing into a 1-liter polyethylene bottle that is two-thirds full of water and cooled in an ice-bath. For one liter of NH<sub>4</sub>OH, specific gravity 0.90, the contents of a 6-ounce lecture bottle are required.

**Silicon Dioxide Standard Solution, (1 ml. = 0.01 mg. SiO<sub>2</sub>).**—Accurately weigh 0.1000 g. of dried, pure silicon dioxide into a platinum crucible. Mix thoroughly with 1 g. of Na<sub>2</sub>CO<sub>3</sub>, cover and fuse the mixture. Cool the melt, dissolve in hot water, transfer to a 1-liter volumetric flask and dilute to volume. Store in a polyethylene bottle. Pipet 50 ml. of this stock solution into a 500-ml. volumetric flask and dilute to volume. Store in a polyethylene bottle.

**Preparation of the Standard Curve.**—Pipet 2-, 5-, 10-, 20-, 30-, 40-, and 50-ml. portions of the SiO<sub>2</sub> standard solution into 100-ml. volumetric flasks. Dilute to

<sup>1</sup> Lundell, G. E. F. and Knowles, H. B., J. Amer. Ceram. Soc., 10, 829, 1927.

about 90 ml and pipet 1 ml of ammonium molybdate solution into each flask mix and record the time Exactly 15 minutes later pipet 4 ml of 10% tartaric acid solution into each flask mix and add with a pipet 1 ml of reductant solution Record the time Dilute the solutions to volume and mix Let the solutions stand 30 minutes Measure the absorbance of the solutions against a reagent blank at 650  $m\mu$  Plot the absorbance against the mg of  $SiO_2$

**Procedure**—This procedure is designed to eliminate the need for the second dehydration in the gravimetric silicon determination Determine the silicon on a 1 g sample using a single dehydration as directed in the first two paragraphs of the Regular Procedure for silicon Dilute the filtrate to 250 ml in a volumetric flask Unless the determination is made immediately store the solution in a clean plastic bottle Pipet 25 ml of the solution into a 100 ml volumetric flask Put 25 ml of water in another 100 ml volumetric flask for a sample blank Place a small piece of Congo Red indicator paper in each flask Neutralize the HCl in the sample by adding silica free  $NH_4OH$  dropwise with a plastic dropper counting the drops Add the same number of drops of silica free  $NH_4OH$  to the blank Acidify the blank dropwise with 1:3 HCl Acidify the sample with 1:4  $H_2SO_4$  Carefully neutralize the sample and the blank dropwise with 1:4 silica free  $NH_4OH$  Shake the flask during this addition because the Congo Red paper changes color slowly to red (pH 5) upon addition of the last required drop Pipet a measured volume (e.g. 30 ml) of the  $SiO_2$  standard solution into a 100 ml volumetric flask and put about the same volume of water in another 100 ml volumetric flask as a blank for this standard Adjust the volumes of all 4 flasks to about 90 ml

Pipet 1 ml of ammonium molybdate solution into each flask and mix Record the time of each addition Exactly 15 minutes after the addition of the ammonium molybdate solution pipet 4 ml of 10% tartaric acid solution into each flask mix and add with a pipet one ml of the reductant solution Record the time Dilute to volume mix and let the solutions stand 30 minutes or a little longer Read the absorbance of the solutions against their respective blanks at 650  $m\mu$  Determine the weight of  $SiO_2$  from the standard curve If the standard gives an unsatisfactory result a new reductant solution must be prepared and the determination repeated on a second aliquot

$$\text{Per cent } SiO_2 = \frac{\text{Wt } SiO_2 \times 1000}{\text{Wt sample}}$$

This %  $SiO_2$  plus that obtained by the single dehydration gravimetric determination equals the total percentage of  $SiO_2$

#### DETERMINATION OF CALCIUM AND MAGNESIUM ( $CaO + MgO$ )

**Reagents** Ammonia Ammonium Chloride Buffer—Dissolve 67.5 g of ammonium chloride in 250 ml of water Add 570 ml of  $NH_4OH$  and dilute to one liter with water Store in a polyethylene bottle

**Calcium Standard Solution** (1 ml = 1 mg  $CaO$ )—This standard solution should be prepared from the purest calcium carbonate available Dry at 110 C for 3 hours and accurately weigh 1.7848 g Dissolve in the minimum amount of 1:1 HCl and dilute to one liter with water

**0.0269 M EDTA Standard Solution** (Ethylenediaminetetraacetic Acid Disodium Salt) (1 ml = 1.50 mg  $CaO$ )—Accurately weigh 10 g of the reagent dissolve and

dilute to one liter with water. Allow to stand overnight and filter into a polyethylene bottle. Standardize this solution by pipetting accurately 25 ml. of the standard calcium solution and 5 ml. of the stock magnesium solution into a beaker, add 10 ml. of freshly prepared 30% aqueous triethanolamine solution, 0.2 g. of Patton and Reeder indicator and sufficient 5 *N* sodium hydroxide to obtain a pH of 12.5–13 (pHydrion paper). Titrate at once with the EDTA solution to a clear blue end point free of violet color.

$$M_{\text{EDTA}} = \frac{0.0269 \times \text{CaO titer}}{1.50}$$

$$\text{CaO Titer} = \frac{\text{Mg. CaO}}{\text{Ml. EDTA}}$$

$$\text{MgO Titer} = \text{CaO Titer} \times 0.7190.$$

**Magnesium Stock Solution.**—This solution should be prepared from the purest magnesium sulfate-heptahydrate available. Weigh accurately 6.1136 g. Dissolve and dilute to 1 liter with water. (Although this solution is not used as a primary standard, it should be free of contaminants that form complexes with EDTA.)

**Mixed Indicator.** 1. *Naphthol Green B.*—Accurately weigh 0.080 g.

2. *o-Cresolphthalein Complexone.*—Accurately weigh 0.050 g.

3. *Eriochrome Black T.*—Accurately weigh 0.006 g.

4. *Ammonium Chloride.*—Accurately weigh 20.0 g. Mix the four constituents by grinding in a glass or agate mortar.

**Patton and Reeder Indicator.**<sup>3</sup>—[2-hydroxyl-1-(2-hydroxyl-4-sulfo-1-naphthylazo)-3-naphthoic acid] (K and K Laboratories, Incorporated, Long Island City, New York.) Accurately weigh 0.1 g. of the indicator powder and mix by grinding in a glass or agate mortar with 10 g. of Na<sub>2</sub>SO<sub>4</sub>.

**Procedure.**—Weigh accurately a 1.000-g. ground sample into a platinum dish (ideally, an 80-ml. capacity). Add several ml. of water, 15 ml. of HF and 5 ml. of HClO<sub>4</sub>. Swirl gently to mix. With the platinum cover slightly displaced, heat at medium heat until most of the hydrofluoric acid is evaporated. Remove the platinum cover and evaporate to dense fumes of perchloric acid. Cool, rinse the lid and sides of the dish with a small quantity of water and evaporate to dryness. To the residue in the dish, add 1 ml. of HCl and 10 ml. of water. Warm to dissolve the salts and cool. Scrub the lid and dish with a rubber policeman and transfer the contents to a 250-ml. volumetric flask. Dilute to volume and mix thoroughly. Pipet two 100-ml. aliquots into 250-ml. beakers or Erlenmeyer flasks.

**CaO Titration.**—To the first aliquot, add 10 ml. of freshly prepared 30% aqueous triethanolamine solution, 0.2 g. of the Patton and Reeder indicator and adjust the pH to 12.5–13 with 5 *N* sodium hydroxide (pHydrion paper). Titrate at once with EDTA solution to a clear blue end point, free of violet color.

$$\text{Per cent CaO} = \frac{\text{Ml. EDTA} \times \text{CaO titer} \times 250}{\text{Wt. sample}}$$

**CaO Plus MgO Titration.**—Add to the second aliquot 10 ml. of 30% triethanolamine solution, adjust to pH 10–11 with ammonia-ammonium chloride buffer solution (usually 10–15 ml.) and add 0.2 g. of the mixed indicator. Titrate with EDTA

<sup>3</sup> Patton, J., and Reeder, W., *Anal. Chem.*, **28**, 1026, 1956.

to a clear light green end point. Some practice may be required to detect the disappearance of the gray undertone color at this end point. Subtract the ml of EDTA required to titrate the CaO ( $y$  ml) from the total ml of EDTA required to titrate the CaO plus MgO ( $z$  ml). The difference is the volume of EDTA required to titrate the MgO.

$$\text{Per cent MgO} = \frac{\text{Ml EDTA } (z - y) \times \text{MgO titer} \times 250}{\text{Wt sample}}$$

**Interferences** *BaO* Often there is sufficient sulfate present in the glass to precipitate small quantities of BaO and the titrations may be performed in the presence of the BaSO<sub>4</sub>. For amounts of BaO up to 2.0% a separation is recommended as follows. To the residue remaining from the HF/HClO<sub>4</sub> treatment add 1 ml HCl and 10 ml of water. Warm to dissolve the salts and transfer the solution to a 250 ml beaker. Add 100 ml of water. Heat to boiling and add 3 ml of 11 N H<sub>2</sub>SO<sub>4</sub>. Boil for 10 minutes and let stand in a warm place for 1 hour. Filter the BaSO<sub>4</sub> through a fine filter paper containing a small quantity of pulp. Wash with warm water. Cool the filtrate, transfer to a 250 ml volumetric flask and dilute to volume with water. Pipet two 100 ml aliquots and titrate as directed for CaO and CaO + MgO.

*NiO* *CoO*—0.10 g KCN added to the aliquots after the pH adjustments are made will prevent blocking of the indicators by these elements.

*MnO*—The 10 ml of triethanolamine solution added in the routine procedure is sufficient to complex 0.20% MnO.

*ZnO*—0.12% ZnO is masked by 0.20 g KCN added to the aliquots after the pH adjustments are made. Since KCN can affect the green end point color of the mixed indicator, do not add more than 0.20 g.

*PbO*—0.05% PbO will not interfere in these determinations.

#### DETERMINATION OF ALUMINUM (Al<sub>2</sub>O<sub>3</sub>)

**Reagents** EDTA Standard Solution—See page 2236.

0.0269 M Copper Standard Solution—Dissolve 6.7165 g of the purest available CuSO<sub>4</sub> · 5H<sub>2</sub>O in water and dilute to one liter. This reagent should be free of contaminants that form complexes with EDTA. Determine the copper equivalent as follows. Accurately measure 10 ml of EDTA, add 10 drops of PAN indicator, adjust to pH 4.55 with 30% ammonium acetate buffer and titrate with the Cu solution to the first permanent purple end point. The color change at the end point is very distinct from yellow yellow-green through gray to a clear and bright purple.

$$\text{Cu equivalent} = \frac{\text{Ml Cu solution}}{\text{Ml EDTA}}$$

$$M_{\text{Cu}} = \frac{\text{Ml EDTA} \times M_{\text{EDTA}}}{\text{Ml Cu}}$$

$$\text{Al}_2\text{O}_3 \text{ titer} = M_{\text{Cu}} \times 0.05098$$

$$\text{Fe}_2\text{O}_3 \text{ titer} = M_{\text{Cu}} \times 0.07985$$

0.1% PAN Indicator, [1 (2-pyridylazo) 2-naphthol]—A 0.1% solution in ethyl alcohol. This indicator must be prepared fresh daily unless its stability has been established experimentally.

*Procedure.*—Treat the sample, dilute to 250 ml. and pipet two 100-ml. aliquots into 250-ml. beakers as directed in the first paragraph of the Rapid Method for calcium and magnesium.

Add from a buret a measured amount of EDTA solution sufficient to give approximately a 50% excess over the amount required to complex the aluminum and iron (e.g., 5 ml. of EDTA would be adequate for a sample that contains about 1%  $\text{Al}_2\text{O}_3$  and 0.1%  $\text{Fe}_2\text{O}_3$ ). Add 5–10 ml. of 30% ammonium acetate solution (the pH should be between 4 and 5.5—check with pHdriion paper). Boil the solution vigorously for 2–3 minutes, add 10 drops of PAN indicator and titrate the hot solution with the standard copper solution to the first permanent purple color.<sup>4</sup> The sum of iron and aluminum is titrated. The per cent of iron is determined on a separate sample.

Per cent  $\text{Al}_2\text{O}_3$  =

$$\frac{\left[ (\text{Ml. EDTA} \times \text{Cu equiv.}) - \left( \text{ml. Cu} + \frac{\% \text{Fe}_2\text{O}_3 \times 0.004}{\text{Fe}_2\text{O}_3 \text{ titer}} \right) \right] \times \text{Al}_2\text{O}_3 \text{ titer} \times 250}{\text{Wt. sample}}$$

#### Interferences.

$\text{Fe}_2\text{O}_3$ .—Fe is titrated quantitatively. A correction, based on the amount of iron determined to be present, is included in the calculations.

$\text{CaO}$ ,  $\text{MgO}$ ,  $\text{BaO}$ .—The quantities normally found in soda-lime glasses do not interfere at pH 4–5.5. Should Ba and  $\text{SO}_3$  be present in sufficient quantities to form a precipitate of  $\text{BaSO}_4$ , it need not be removed from the solution.

$\text{MnO}$ .—Manganese interferes by giving an indistinct end point if present in amounts greater than 3 mg.

$\text{NiO}$ ,  $\text{CoO}$ ,  $\text{TiO}_2$ ,  $\text{ZrO}_2$ ,  $\text{CuO}$ ,  $\text{ZnO}$ ,  $\text{CdO}$ ,  $\text{PbO}$ ,  $\text{BiO}$ .—These cations will interfere if present in sufficient quantity to be titrated.

#### DETERMINATION OF CHLORIDE (Cl) <sup>5</sup>

*Apparatus.* Potentiometer, such as Rubicon Model No. 2730.

*Silver-Silver Chloride Electrode.*—Prepare the electrode by electroplating a platinum electrode in a potassium cyano-argentate solution containing 36 g. of  $\text{AgNO}_3$  and 43 g. of KCN per liter. Then anodically coat the electrode with silver chloride in a 1% sodium chloride solution. Wash the electrode repeatedly and store in distilled water for several days before use. When not in use, the electrode should be kept in distilled water.

*Saturated Calomel Electrode.*—The electrode must be connected to the solution through a  $\text{NaNO}_3$ -agar gel bridge to prevent contamination by chloride from the calomel electrode.

*Procedure.*—Weigh accurately a 1-g. ground sample and mix with 5.0 g. of anhydrous  $\text{Na}_2\text{CO}_3$  in a platinum crucible. Cover the crucible, fuse the mixture, cool and transfer the melt to a 100-ml. beaker. Cover the beaker with a watch glass and add 10 ml. of 1:1  $\text{HNO}_3$ . Rinse the crucible with 2 ml. of 1:1  $\text{HNO}_3$  into the beaker. Place a magnetic stirring bar in the beaker and stir the mixture with a magnetic stirrer until the melt has disintegrated. A large amount of silica will be suspended in the solution. Rinse the watch glass into the beaker and dilute the sample to about 50 ml.

<sup>4</sup> Cheng, K. L., and Waimuth, F. J., *Chemist Analyst*, 48, 74, 1959.

<sup>5</sup> Kolthoff, I. M., and Kuroda, P. K., *Anal. Chem.*, 23, 1304, 1951.

Connect the silver-silver chloride electrode to the positive terminal and the saturated calomel electrode to the negative terminal of the potentiometer. Place the electrodes in the solution and adjust the magnetic stirrer so that the solution is stirred as vigorously as possible without splashing. Add 0.003 M  $\text{AgNO}_3$  slowly from a 10 ml buret while continuously checking the potential of the electrode pair with the potentiometer. Since the potential vs volume curve undergoes only a slight inflection, the end point is indicated when the potential reaches a predetermined value which will vary with the particular electrodes used. This value is determined by preparing a solution to duplicate a titrated solution (add equivalent amounts of standard solutions of silver and chloride) and measuring the potential using the prepared electrodes (e.g. a set of electrodes prepared in our laboratory gave a potential of 0.2744 volts). Since the reagents used are likely to contain traces of chloride, a blank should be run using the same procedure. Subtract this volume from the total volume of silver nitrate used in the titration. The volume used for the titration of the blank should be considerably smaller than that used for the titration of the sample.

$$\text{Per cent Cl} = \frac{\text{ml AgNO}_3 \times 0.003 \times 0.0355 \times 100}{\text{Wt sample}}$$

#### DETERMINATION OF SODIUM ( $\text{Na}_2\text{O}$ )

**Reagent** Magnesium Uranyl Acetate—Prepare the following solutions

**Solution 1** Uranyl acetate ( $2\text{H}_2\text{O}$ ) 90 g glacial acetic acid 60 g dilute to 1 liter with water

**Solution 2** Magnesium acetate ( $4\text{H}_2\text{O}$ ) 600 g glacial acetic acid 60 g dilute to 1 liter with water

Heat each solution separately to about  $70^\circ\text{C}$  until all the salts are dissolved. Mix the two solutions at this temperature, cool to  $20 \pm 1^\circ\text{C}$ , hold at this temperature for at least 1 hour, then filter through a dry, medium porosity porcelain filtering crucible into a dry bottle. This solution is stable if kept away from direct sunlight. If it is cooled below  $20^\circ\text{C}$  at any time, it must be refiltered.

**Procedure**—Accurately weigh a 0.1 g ground sample into a platinum crucible. Add 1 ml of 1:1  $\text{H}_2\text{SO}_4$ , 5 ml of HF, cover and evaporate to dryness. Remove the cover and expel the sulfuric acid completely. Add 1 ml of 1:1 HCl and 10 ml of water, warm to dissolve the salts and transfer to a 250 ml beaker. (If insoluble barium sulfate is present, filter onto a fine filter paper and wash with water.) Evaporate to a volume of 5 ml and add one ml of the magnesium uranyl acetate solution per mg of Na present. Cool the solution in a water bath maintained at  $20 \pm 1^\circ\text{C}$  and stir vigorously for 30 to 60 minutes. Filter through a medium porosity glass filtering crucible. Scrub the beaker carefully and wash the precipitate with four to six 5 ml portions of 95% ethyl alcohol that has been freshly saturated at  $20^\circ\text{C}$  with the triple acetate salt. Dry at  $105^\circ\text{C}$  for 30 minutes, cool in a desiccator and weigh as  $\text{NaMg}(\text{UO}_2)_3(\text{C}_2\text{H}_3\text{O}_2)_9 \cdot 6\frac{1}{2}\text{H}_2\text{O}$ .

$$\text{Per cent Na}_2\text{O} = \frac{\text{Wt NaMg}(\text{UO}_2)_3(\text{C}_2\text{H}_3\text{O}_2)_9 \cdot 6\frac{1}{2}\text{H}_2\text{O} \times 0.02058 \times 100}{\text{Wt sample}}$$

#### DETERMINATION OF POTASSIUM ( $\text{K}_2\text{O}$ )

**Procedure**—Accurately weigh a 0.5 g ground sample into a platinum dish. Dissolve the sample and remove the Ba, As, Sb and  $\text{R}_2\text{O}_3$  group as directed in the first three paragraphs of the Regular Procedure for calcium.

Acidify the filtrate from the  $R_2O_3$  group with 1:1 HCl, heat to boiling and add 10 ml. of a saturated solution of ammonium oxalate. Precipitate the calcium by adding  $NH_4OH$  dropwise until the solution turns yellow. Boil 5–10 minutes, let cool and add sufficient  $NH_4OH$  to make the solution 5% by volume. Add 4 ml. of a 5% 8-hydroxyquinoline solution. Heat to 60–70°C., stir and continue heating for 10–15 minutes. Do not boil. Let stand in a cold water bath for at least one hour. Filter the combined calcium and magnesium precipitate through a fine filter paper. Wash the precipitate about 10 times with 1:40  $NH_4OH$ . Discard the precipitate and transfer the filtrate to a glazed porcelain casserole. Separate the alkali sulfates as directed in the Regular Procedure for total alkalis.

Filter the water solution of the alkali sulfates into a small porcelain evaporating dish, add 5 ml. of HCl and sufficient 10% chloroplatinic acid solution to react with the potassium. Dilute the solution with enough water to dissolve any precipitate completely upon heating. Evaporate on a steam bath until the solution is syrupy but solidifies on cooling. Do not evaporate to dryness. Add 20 ml. of 80% ethyl alcohol. Decant through a coarse filter paper and wash by decantation with 80% ethyl alcohol, crushing the crystals with a small glass rod. Wash by decantation until the filtrate becomes colorless. The volume of the filtrate should not exceed 50–75 ml. The residue should be golden yellow. It is not necessary to transfer the precipitate to the filter paper. Dry the dish and filter paper for a few minutes to remove the adhering alcohol. Dissolve the precipitate on the filter paper and that remaining in the dish with hot water. Transfer to a 150-ml. beaker, dilute to about 75 ml., add 1 ml. of HCl and 0.5 g. of magnesium ribbon for each 0.2 g. of potassium present. When the effervescence ceases, add 5 ml. of HCl. After the magnesium ribbon has dissolved, boil the solution for 5 minutes. Cool, filter through a medium filter paper and wash with hot water until free from chlorides. Place the paper and precipitate in a weighed platinum crucible. Heat until the carbon is destroyed and then ignite to constant weight in a muffle furnace at 900°C. Cool in a desiccator and weigh as metallic Pt.

$$\text{Per cent } K_2O = \frac{\text{Wt. Pt} \times 0.4825 \times 100}{\text{Wt. sample}}$$

#### DETERMINATION OF SULFUR (TOTAL $SO_3$ )

**Apparatus.**—High frequency induction apparatus for combustion analyses, such as used for the determination of sulfur in steel.

**Reagent.** Potassium Iodate Standard Solution, (1 ml. = 0.1 mg. S).—Accurately weigh 0.2069 g. of  $KIO_3$ , dissolve and dilute to exactly 1 liter with water. This solution does not require further standardization.

**Procedure.**—Accurately weigh a 0.25-g. ground sample into a zirconia cupelet. Mix thoroughly with 1 g. of Plast-iron then cover evenly with 0.5 g. of granular tin. Cover the cupelet with a zirconia sulfur cap and place the sample in the apparatus. Operate the equipment for the combustion of the sample as directed in the manufacturer's instructions. Upon combustion of the sample (usually 2.5 to 3 minutes),  $SO_2$  gas is absorbed and titrated with  $KIO_3$ . The determination of a blank on the apparatus and reagents is very important.

$$\text{Per cent } SO_3 = \frac{\text{Ml. } KIO_3 \times \text{S titer} \times 2.497 \times 100}{\text{Wt. sample}}$$



## COLORING ELEMENTS

Only absorption photometric methods are given in this section because they are generally the best methods for the low concentrations of these elements normally encountered. Iron may occur in larger concentrations in highly colored glasses and then the procedure given for total iron in the section Analysis of Clays and Feldspars (page 2262) can be used. There are many photometers and spectrophotometers of varying degrees of complexity and with a wide range of prices available for this type of determination. For this reason no specific directions are given for operation of the instrument in the following procedures. The manufacturers' directions for operation of their specific instruments should be used. Any colored solution which is to be measured in a photometer should be examined carefully for turbidity or the presence of an unusual color hue before the measurement is made because interferences frequently can be detected in this way.

DETERMINATION OF CHROMIUM ( $\text{Cr}_2\text{O}_3$ )

**Reagents Required** Chromium Standard Solution (1 ml = 0.020 mg  $\text{Cr}_2\text{O}_3$ )—Accurately weigh 0.0387 g of dry primary standard  $\text{K}_2\text{Cr}_2\text{O}_7$ . Dissolve and dilute to exactly one liter with water.

**Diphenylcarbazide**—Dissolve 0.0500 g of diphenylcarbazide and 0.80 g of phthalic anhydride in 100 ml of ethyl alcohol. This solution should be prepared the same day that it is used.

**Preparation of the Standard Curve**—Pipet 1, 2, 3, 4, and 5 ml portions of the standard chromium solution into 250 ml volumetric flasks. Dilute partially with water and add 10 ml of 1:1  $\text{H}_2\text{SO}_4$  plus 10 ml of diphenylcarbazide solution. Let stand 5 minutes and measure the absorbance of the solution at 540  $\text{m}\mu$  against a reagent blank. Plot the absorbance against the mg of  $\text{Cr}_2\text{O}_3$ .

**Procedure**—Accurately weigh a ground sample of such size that it will contain no more than 0.1 mg of  $\text{Cr}_2\text{O}_3$  into a small platinum dish. Add 5 ml of  $\text{HNO}_3$  and 15 ml  $\text{HF}$  and evaporate carefully to dryness. Add 10 ml of 1:1  $\text{H}_2\text{SO}_4$  evaporate to strong fumes of sulfuric acid, cool and add 20 ml of water. Warm until the soluble salts are in solution and transfer to a beaker. Filter onto a fine filter paper if  $\text{BaSO}_4$  is present and wash with hot water. Heat to boiling and add 2 ml of 1%  $\text{AgNO}_3$  solution and 10 ml of a freshly prepared 15% ammonium persulfate solution. If traces of  $\text{Vn}$  are present add one drop of 1:1  $\text{HCl}$ . Boil 15 minutes to decompose the excess persulfate. Cool and filter into a 250 ml volumetric flask. Dilute partially with water, add 10 ml of diphenylcarbazide solution and dilute to volume. Let the solution stand 5 minutes and read the absorbance at 540  $\text{m}\mu$  against a reagent blank. Determine the weight of  $\text{Cr}_2\text{O}_3$  from the standard curve.

$$\text{Per cent } \text{Cr}_2\text{O}_3 = \frac{\text{Wt } \text{Cr}_2\text{O}_3 \times 100}{\text{Wt sample}}$$

DETERMINATION OF COBALT—( $\text{CoO}$ )

**Reagents Required** Cobalt Standard Solution, (1 ml = 0.01 mg  $\text{CoO}$ )—Accurately weigh 0.3750 g of high purity  $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$  dissolve and dilute to one liter with water. Pipet 100 ml of this solution into a 1 liter volumetric flask and dilute to the mark to obtain the standard solution.

**Nitroso R Salt**—Dissolve 0.50 g of nitroso R salt in water and dilute to 100 ml. Keep in the dark as the solution slowly decomposes in the daylight.

**Sulfuric-Phosphoric Acid Mixture.**—Prepare 500 ml. of a water solution that contains 75 ml. of  $\text{H}_2\text{SO}_4$  and 75 ml. of  $\text{H}_3\text{PO}_4$ .

**Preparation of the Standard Curve.**—Pipet 2-, 4-, 6-, 8-, and 10-ml. portions of the standard cobalt solution into 150-ml. beakers. Add 6 ml. of 1:1  $\text{HCl}$ , 20 ml. of hot water, 2 ml. of 1:1  $\text{HNO}_3$ , 2.5 ml. of the sulfuric-phosphoric acid mixture and boil for 5 minutes. Add 35 ml. of 4 *M* sodium acetate solution (the pH should be 5.5–6.5) and 2 ml. of the nitroso-R-salt solution. Boil for exactly one minute, add 10 ml. of  $\text{HNO}_3$  and boil again for at least one but not more than two minutes. Cool rapidly and transfer the solutions to 100-ml. volumetric flasks. Dilute to volume with water and read the absorbance at 500  $m\mu$  against a reagent blank. Plot the absorbance against the mg. of  $\text{CoO}$ .

**Procedure.**—Accurately weigh a ground sample which will contain no more than 0.1 mg. of  $\text{CoO}$  into a small platinum dish. Add 1 ml. of 1:1  $\text{H}_2\text{SO}_4$ , 15 ml. of  $\text{HF}$  and evaporate to dryness. Add 6 ml. of 1:1  $\text{HCl}$ , 20 ml. of hot water and heat until the soluble salts are dissolved. Filter if  $\text{BaSO}_4$  is present. Transfer the solution to a 150-ml. beaker, add 2 ml. of 1:1  $\text{HNO}_3$ , 2.5 ml. of the phosphoric-sulfuric acid mixture and boil for 5 minutes. Add 35 ml. of 4 *M* sodium acetate solution (the pH of the solution should be 5.5–6.5) and 2 ml. of the nitroso-R-salt solution. Boil for exactly one minute, add 10 ml. of  $\text{HNO}_3$ , and boil again for at least one but not more than two minutes. This decomposes the nitroso-R-salt complexes of copper and nickel. Cool rapidly and transfer to a 100-ml. volumetric flask. Dilute to volume with water. If the solution is turbid, filter through two sheets of fine filter paper. Read the absorbance at 500  $m\mu$  against a reagent blank. Determine the weight of  $\text{CoO}$  from the standard curve.

$$\text{Per cent CoO} = \frac{\text{Wt. CoO} \times 100}{\text{Wt. sample}}$$

#### DETERMINATION OF COPPER—CuO

**Reagents Required.** Copper Standard Solution, (1 ml. = 0.01 mg.  $\text{CuO}$ ).—Accurately weigh 3.1392 g. of the purest  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  available. Dissolve in water and dilute to one liter. Pipet 10 ml. of this solution and dilute to exactly one liter with water to obtain the standard solution.

**Cuprizone.**—(Bis-cyclohexanone oxalydihydrazone) (G. Frederick Smith Chemical Co., Columbus, Ohio). Dissolve 0.100 g. of cuprizone in 20 ml. of hot ethyl alcohol.

**Preparation of the Standard Curve.**—Pipet 2-, 4-, 6-, 8-, and 10-ml. portions of the standard solution into 150-ml. beakers. Add 1 ml. of 1:1  $\text{H}_2\text{SO}_4$ . Adjust the solution to pH 7 with 1:1  $\text{NH}_4\text{OH}$  (pHydrion paper) and add 2 ml. of a 10% solution of citric acid. Adjust the pH to  $8.5 \pm 0.2$  pH units (use a pH meter) with 6 *N*  $\text{NaOH}$ . Add 1 ml. of cuprizone solution and dilute to exactly 100 ml. with water. Measure the absorbance of the solution at 606  $m\mu$  against a reagent blank. Plot the absorbance of the solution against the mg. of  $\text{CuO}$ .

**Procedure.**—Accurately weigh a ground sample of such size that it will contain no more than 0.1 mg. of  $\text{CuO}$  into a small platinum dish. Add 5 ml. of  $\text{HNO}_3$ , 15 ml. of  $\text{HF}$  and evaporate carefully to dryness. Add 10 ml. of 1:1  $\text{H}_2\text{SO}_4$  and evaporate to heavy fumes. Cool and add 25 ml. of water. Warm slightly and transfer to a 150-ml. beaker. Dilute to approximately 100 ml. and heat until the soluble salts are dissolved. Pass in a current of hydrogen sulfide as the solution cools. Discontinue the flow of gas and filter through a fine filter paper that contains a small quantity of pulp, keeping the paper wet. Wash with a 1% sulfuric

acid solution saturated with hydrogen sulfide and discard the filtrate. Dissolve the precipitate at once from the paper with 5 ml of 1:1  $\text{HNO}_3$  into a 100 ml beaker. Wash the paper twice with small amounts of hot water. Add 1 ml of 1:1  $\text{H}_2\text{SO}_4$  and evaporate to dryness. Dissolve the residue with 1 ml of 1:1  $\text{H}_2\text{SO}_4$  and 25 ml of warm water. Cool and neutralize the solution with 1:1  $\text{NH}_4\text{OH}$  to a pH of 7 (pH-dion paper). Add 2 ml of a 10% solution of citric acid. Adjust the pH to  $8.5 \pm 0.2$  pH units (use a pH meter) with 6 N NaOH. Add 1 ml of cuprizone solution, transfer to a 100 ml volumetric flask and dilute to volume. Read the absorbance of the solution at 606 m $\mu$  against a reagent blank. Determine the weight of CuO from the standard curve.

$$\text{Per cent CuO} = \frac{\text{Wt CuO} \times 100}{\text{Wt sample}}$$

#### DETERMINATION OF TOTAL IRON— $\text{Fe}_2\text{O}_3$

**Reagents Required** Iron Standard Solution, (1 ml = 0.01 mg  $\text{Fe}_2\text{O}_3$ )—Accurately weigh 0.6994 g of primary standard electrolytic iron (Standard Sample Co. Ames, Iowa). Warm in the minimum amount of 1:1 HCl until dissolved and dilute with water to exactly one liter. Pipet 10 ml of this stock solution, add 2 ml of HCl and dilute to one liter with water to obtain the standard solution.

**o-Phenanthroline**—Dissolve 0.5 g of o-phenanthroline in 25 ml of ethyl alcohol and 75 ml of water.

**Preparation of the Standard Curve**—Pipet 25, 50, 75 and 100 ml portions of the iron standard solution into 250 ml volumetric flasks. Add 4 ml of 1:1 HCl, 3 ml of 10% hydroxylamine hydrochloride solution, 25 ml of 2 M sodium acetate solution, 3 ml of o-phenanthroline solution and dilute to volume with water. Measure the absorbance of the solution at 510 m $\mu$  against a reagent blank. Plot the absorbance against the mg of  $\text{Fe}_2\text{O}_3$ .

**Procedure**—Accurately weigh a ground sample which will contain no more than one mg of  $\text{Fe}_2\text{O}_3$  into a small platinum dish. Add one ml of 1:1  $\text{H}_2\text{SO}_4$  and 15 ml of HF and evaporate to dryness. Cool and add 5 ml of 1:1 HCl and 20 ml of hot water. (Zinc interferes. If it is present, separate the  $\text{R}_2\text{O}_3$  group as directed in the third paragraph of the Regular Procedure for calcium except save the precipitate. Place the paper and precipitate in the precipitation beaker, add 5 ml of 1:1 HCl, macerate the paper and warm to dissolve the precipitate. Filter onto a coarse filter paper, wash 5 times with hot water, cool the filtrate and transfer to a 250 ml volumetric flask.) Warm until the soluble salts are in solution and transfer to a 250 ml volumetric flask, filtering if  $\text{BaSO}_4$  is present.

Dilute partially with water, add 3 ml of 10% hydroxylamine hydrochloride, 25 ml of 2 M sodium acetate buffer, 3 ml of o-phenanthroline solution and dilute to volume with water. Measure the absorbance of the solution at 510 m $\mu$  against a reagent blank. Determine the weight of  $\text{Fe}_2\text{O}_3$  from the standard curve.

$$\text{Per cent Fe}_2\text{O}_3 = \frac{\text{Wt Fe}_2\text{O}_3 \times 100}{\text{Wt sample}}$$

#### DETERMINATION OF MANGANESE—MnO

**Reagents Required** Manganese Standard Solution, (1 ml = 0.05 mg MnO)—Accurately weigh 0.0194 g of electrolytic manganese metal. Warm until dissolved in the minimum amount of 1:1  $\text{HNO}_3$ , boil to remove the oxides of nitrogen, cool and dilute to exactly 500 ml with water.

**Preparation of the Standard Curve.**—Pipet 2-, 5-, 10-, 15-, and 20-ml. portions of the manganese standard solution into beakers. Add 10 ml. of 1:1  $\text{H}_2\text{SO}_4$ , 7 ml. of  $\text{HNO}_3$  and 20 ml. of water. Boil to remove the oxides of nitrogen and add 2 ml. of a 1% solution of  $\text{AgNO}_3$  and 10 ml. of a freshly prepared 10% solution of ammonium persulfate. Boil for several minutes, cool, transfer to a 250-ml. volumetric flask and dilute to volume with water. Measure the absorbance of the solution at 548  $\text{m}\mu$  against a reagent blank. Plot the absorbance against the mg. of  $\text{MnO}$ .

**Procedure.**—Accurately weigh a ground sample which will contain no more than one mg. of  $\text{MnO}$  into a small platinum dish. Add one ml. of 1:1  $\text{H}_2\text{SO}_4$ , 15 ml. of  $\text{HF}$  and evaporate to strong fumes of sulfuric acid. Fume for 5 minutes and cool.

Add 7 ml. of  $\text{HNO}_3$  and 20 ml. of water, warm slightly and transfer to a 250-ml. beaker, filtering if  $\text{BaSO}_4$  is present. Add 10 ml. of 1:1  $\text{H}_2\text{SO}_4$  and boil to remove the oxides of nitrogen. Add 2 ml. of 1%  $\text{AgNO}_3$ , 10 ml. of a freshly prepared 10% solution of ammonium persulfate and boil for several minutes. Cool rapidly, transfer to a 250-ml. volumetric flask and dilute to volume with water. Read the absorbance at 548  $\text{m}\mu$  against a reagent blank. Determine the weight of  $\text{MnO}$  from the standard curve.

$$\text{Per cent MnO} = \frac{\text{Wt. MnO} \times 100}{\text{Wt. sample}}$$

#### DETERMINATION OF NICKEL—NiO

**Reagents Required.** Nickel Standard Solution, (1 ml. = 0.01 mg.  $\text{NiO}$ ).—Accurately weigh 0.3760 g. of the purest  $\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$  available. Dissolve and dilute to exactly one liter with water. Pipet 100 ml. of this solution and dilute to one liter to obtain the standard solution.

**Dimethylglyoxime.**—Prepare a 1% solution of the salt in ethyl alcohol.

**Preparation of the Standard Curve.**—Pipet 5-, 10-, 15-, and 20-ml. portions of the nickel standard solution into 150-ml. beakers. Add 15 ml. of 1:1  $\text{HCl}$ , 10–15 ml. of water, 5 ml. of a 20% solution of citric acid and 16 ml. of  $\text{NH}_4\text{OH}$ . The pH should be between 9 and 10. Transfer to a 100-ml. volumetric flask, add 5 ml. of bromine water, mix well, add 3 ml. of dimethylglyoxime solution and dilute to volume with water. Measure the absorbance of the solution at 446  $\text{m}\mu$  against a reagent blank. Plot the absorbance against the mg. of  $\text{NiO}$ .

**Procedure.**—Accurately weigh a ground sample which will contain no more than 0.2 mg. of  $\text{NiO}$  into a small platinum dish. Add 1 ml. of 1:1  $\text{H}_2\text{SO}_4$ , 15 ml. of  $\text{HF}$  and evaporate to dryness. Add 15 ml. of 1:1  $\text{HCl}$ , 15 ml. of water and warm until the soluble salts are dissolved. Transfer the solution to a 150-ml. beaker, filtering if  $\text{BaSO}_4$  is present. Add 5 ml. of a 20% solution of citric acid and 16 ml. of  $\text{NH}_4\text{OH}$ . The pH should be between 9 and 10. Place the solution in a 100-ml. volumetric flask and cool rapidly. Add 5 ml. of bromine water, mix well, add 3 ml. of dimethylglyoxime solution and dilute to volume with water. Read the absorbance at 446  $\text{m}\mu$  against a reagent blank. Determine the weight of  $\text{NiO}$  from the standard curve.

$$\text{Per cent NiO} = \frac{\text{Wt. NiO} \times 100}{\text{Wt. sample}}$$

DETERMINATION OF TITANIUM— $\text{TiO}_2$ 

**Reagents Required** Titanium Standard Solution (1 ml 0.1 mg  $\text{TiO}_2$ )—Accurately weigh 0.0000 g of the purest available dry titanium dioxide. Add 50 ml of 1:1  $\text{H}_2\text{SO}_4$  and evaporate to heavy fumes of sulfuric acid. Cool this solution and add to 300 ml of water and dilute to exactly 500 ml.

**Preparation of the Standard Curve**—Pipet 2, 4, 6, 8, and 10 ml portions of the titanium standard solution into 100 ml volumetric flasks. Add 10 ml of 1:1  $\text{H}_2\text{SO}_4$ , dilute partially with water, add 5 ml of 3% hydrogen peroxide and dilute to volume with water. Measure the absorbance of the solution at 410  $\text{m}\mu$  against a reagent blank. Plot the absorbance against the  $\text{mg}$  of  $\text{TiO}_2$ .

**Procedure**—Accurately weigh a ground sample which will contain no more than one  $\text{mg}$  of  $\text{TiO}_2$  into a small platinum dish. Add 10 ml of 1:1  $\text{H}_2\text{SO}_4$ , 15 ml of  $\text{HF}$  and evaporate to strong fumes of sulfuric acid. Cool and add 15–20 ml of water. Transfer to a 150 ml beaker and warm until the soluble salts are dissolved.

Place in a 100 ml volumetric flask, filtering if  $\text{BaSO}_4$  is present. Dilute partially with water, add 5 ml of 3% hydrogen peroxide and complete the dilution to volume. Read the absorbance at 410  $\text{m}\mu$  against a reagent blank. Determine the weight of  $\text{TiO}_2$  from the standard curve.

$$\text{Per cent TiO}_2 = \frac{\text{Wt TiO}_2 \times 100}{\text{Wt sample}}$$

## THE ANALYSIS OF LEAD GLASSES

The following procedures are applicable to silicate glasses that contain lead, barium, calcium, magnesium, zirconium, sodium and/or potassium as major constituents and up to 4%  $\text{CaO}$ , 3%  $\text{Al}_2\text{O}_3$ , 1%  $\text{SO}_3$ , 1%  $\text{F}$ , 0.5%  $\text{Cl}$ , 0.5%  $\text{Sb}_2\text{O}_3$ , 0.5%  $\text{Fe}_2\text{O}_3$ , 0.25%  $\text{As}_2\text{O}_3$  and 0.1%  $\text{TiO}_2$ .

DETERMINATION OF SILICON ( $\text{SiO}_2$ )

**Procedure**—Accurately weigh a 1 g ground sample into a 30 ml platinum crucible and mix thoroughly with 6 g of  $\text{Na}_2\text{CO}_3$  and 0.2 g of  $\text{KNO}_3$ . Cover the crucible and heat over a Meker burner at the lowest temperature possible to obtain a fusion. Transfer the melt to a 150 ml beaker. Add 75 ml of hot water and let stand at 30–40°C for about four hours. Filter the insoluble material onto a coarse filter paper and wash 10 times with a hot 5%  $\text{Na}_2\text{CO}_3$  solution. Collect the filtrate and washings in a porcelain casserole (No. 1). Dissolve the acid-soluble material from the filter paper with hot 10%  $\text{HNO}_3$  into a porcelain casserole (No. 2), washing the filter paper with hot water. Add carefully 25 ml of  $\text{HCl}$  to casserole No. 1 and 10 ml of  $\text{HNO}_3$  to casserole No. 2. Evaporate the solutions to dryness on a hot plate, continue heating until the smell of the acids has disappeared, then cool. To casserole No. 1 add 10 ml of  $\text{HCl}$  and to casserole No. 2 add 10 ml of  $\text{HNO}_3$ . Add 50 ml of hot water to each casserole, heat for 5–10 minutes to dissolve the salts and filter onto coarse filter papers. Wash 10 times with hot water and place both filter papers and precipitates in an unweighed platinum crucible.

Return the filtrates to their respective casseroles and again evaporate to dryness. Add to casserole No. 1 3 ml of  $\text{HCl}$  and to casserole No. 2 3 ml of  $\text{HNO}_3$ . Add 25 ml of hot water to each casserole, warm to dissolve the soluble salts, filter through

coarse filter papers and wash 5 times with warm water. Save the filtrate from casserole No. 1 for the determination of total sulfate. Place both filter papers in the platinum crucible. Char carefully and ignite in a muffle furnace to constant weight at 1000–1050°C. Cool in a desiccator and weigh. Moisten the contents with water, add 6 drops of 1:1  $\text{H}_2\text{SO}_4$  and 10 ml. of HF. Evaporate to dryness and reignite for 5 minutes at 1000°C. Cool in a desiccator and weigh. The loss in weight is  $\text{SiO}_2$ .

$$\text{Per cent SiO}_2 = \frac{\text{Wt. SiO}_2 \times 100}{\text{Wt. sample}}$$

#### DETERMINATION OF SULFUR (TOTAL $\text{SO}_3$ )

**Procedure.**—Determine total sulfate on the filtrate from casserole No. 1, above. Proceed as directed in the Regular Procedure for sulfur, beginning with the first paragraph.

#### DETERMINATION OF LEAD ( $\text{PbO}$ ) AND BARIUM ( $\text{BaO}$ )

**Regular Procedures—High Pb Content.** **PbO + BaO.**—Accurately weigh a 1.0000-g. ground sample into a platinum dish. Add 5 ml.  $\text{HNO}_3$ , 15 ml. HF, 5 ml. of  $\text{H}_2\text{SO}_4$ , cover and heat until fumes of sulfuric acid appear. Remove the cover, rotate the contents of the dish and continue to fume lightly for several minutes. Cool and replace the cover. Add 25 ml. of cold water, heat and transfer to a 250-ml. beaker. Dilute to about 100 ml., boil gently for 30 minutes. Cool, add an equal volume of alcohol and let stand overnight.

Filter on a weighed fine porosity porcelain filtering crucible and wash 10 times with 1%  $\text{H}_2\text{SO}_4$ . Save the filtrate for the determination of total  $\text{R}_2\text{O}_3$ . Wash the precipitate several times with ethyl alcohol. Place the crucible in a muffle furnace and heat gradually to constant weight at 500–600°C. Cool in a desiccator and weigh as  $\text{BaSO}_4 + \text{PbSO}_4$ .

**BaO.**—Accurately weigh a 1.0000-g. ground sample into a platinum dish. Treat the sample and remove the lead by electrolytic deposition as directed in the following section (Determination of Lead and Barium) (do not weigh). Determine the barium in the electrolyte, as directed in the following section (BaO), using 5–10 ml. of 1:1  $\text{H}_2\text{SO}_4$ .

$$\text{Per cent PbO} = \frac{(\text{Wt. PbSO}_4 + \text{BaSO}_4) - \text{wt. BaSO}_4 \times 0.7360 \times 100}{\text{Wt. sample}}$$

$$\text{Per cent BaO} = \frac{\text{Wt. BaSO}_4 \times 0.6570 \times 100}{\text{Wt. sample}}$$

#### DETERMINATION OF LEAD ( $\text{PbO}$ ) AND BARIUM ( $\text{BaO}$ )

**Alternate Procedures—Low Pb Content.** **PbO.**—Accurately weigh a ground sample that will contain not more than 0.1 g. of lead into a platinum dish. Add 5 ml. of  $\text{HNO}_3$ , 15 ml. of HF and evaporate to dryness. Cool, add 5 ml. of  $\text{HNO}_3$  and again evaporate to dryness. Add 20 ml. of  $\text{HNO}_3$ , 25 ml. of hot water, and warm with stirring until the residue is dissolved. Transfer to an electrolytic beaker and dilute to 100 ml. with water. The concentration of  $\text{HNO}_3$  should be about 20%. Heat to approximately 50°C. and place in an electrodeposition apparatus that contains a weighed platinum gauze anode. Adjust the current to 0.5 ampere for

15 minutes then to 10 ampere for 15 minutes then to 3 amperes and begin stirring of the solution. Test for completeness of deposition by adding water continuing the electrolysis for 10-15 minutes and observing whether further deposition occurs on the anode. Without interrupting the current lower the beaker while washing the anode with water. Reserve the electrolyte for the determination of barium. Dry the anode at 105° C for 30 minutes cool in a desiccator and weigh as PbO.

$$\text{Per cent PbO} = \frac{\text{Wt PbO}_2 \times 0.931 \times 100}{\text{Wt sample}}$$

NOTE—To clean the anode place it in a beaker with warm 1:3 HNO<sub>3</sub> and add a small amount of hydrogen peroxide or alcohol.

BaO—Filter the electrolyte through a coarse filter paper into a 400 ml beaker. Wash 5 times with warm water. Add several drops of bromine water boil to volatilize the excess and neutralize the solution with NH<sub>4</sub>OH to the yellow color of methyl red indicator. Add HCl dropwise until the solution turns red then add 6 drops excess acid. Heat the solution to boiling and add slowly 3-5 ml of 1:1 H<sub>2</sub>SO<sub>4</sub>. Boil for 10-15 minutes digest for 2-3 hours at 50-60° C. Filter on a weighed fine porosity porcelain filtering crucible and wash the precipitate 6-10 times with water. Ignite the precipitate to a constant weight in a muffle furnace at 900° C. Cool in a desiccator and weigh as BaSO<sub>4</sub>.

$$\text{Per cent BaO} = \frac{\text{Wt BaSO}_4 \times 0.6570 \times 100}{\text{Wt sample}}$$

#### DETERMINATION OF TOTAL R<sub>2</sub>O<sub>3</sub> (Fe<sub>2</sub>O<sub>3</sub>, Al<sub>2</sub>O<sub>3</sub>, TiO<sub>2</sub>, ZrO, MnO and CeO)

Procedure—If the alternate procedure (preceding section) was used determine the R<sub>2</sub>O<sub>3</sub> on the evaporated filtrate from a separate 1 g sample from which Pb + Ba have been removed as directed in the Regular Procedure for lead and barium. If the regular procedure was used evaporate the filtrate remaining after the PbO + BaO determination to dryness.

To the residue add 15 ml of HCl and dilute to 100 ml with hot water. (When antimony and arsenic are present separate them as directed in the second paragraph of the Regular Procedure for calcium.) Add 10 ml of bromine water and boil until the bromine is volatilized. Add several drops of methyl red indicator and precipitate the R<sub>2</sub>O<sub>3</sub> by adding NH<sub>4</sub>OH dropwise until the solution turns yellow. Add 5-10 drops of NH<sub>4</sub>OH in excess and boil for one minute to coagulate the precipitate. Cool slightly and add 5 ml of 3% H<sub>2</sub>O<sub>2</sub> to precipitate the rare earths. Let stand for 30 minutes filter through a coarse filter paper and wash the precipitate with a 2% ammonium chloride solution. Save the filtrate for the determination of calcium. Place the precipitate in a weighed platinum crucible char slowly and ignite to constant weight in a muffle furnace at 900-1000° C. Cool in a desiccator and weigh as total R<sub>2</sub>O<sub>3</sub>. Save the precipitate for the zirconium determination.

$$\text{Per cent R}_2\text{O}_3 = \frac{\text{Wt R}_2\text{O}_3 \times 100}{\text{Wt sample}}$$

*DETERMINATION OF CALCIUM (CaO)*

*Procedure.*—Precipitate the calcium as an oxalate in the filtrate from the total  $R_2O_3$  determination as directed in the Regular Procedure for calcium, beginning with the fourth paragraph.

*DETERMINATION OF MAGNESIUM (MgO)*

*Procedure.*—Determine the magnesium in the combined filtrates from the calcium determination as directed in the Regular Procedure for magnesium.

*DETERMINATION OF SODIUM (Na<sub>2</sub>O)*

*Procedure.*—Determine the total alkali sulfates in the filtrate from the magnesium determination as directed in the Regular Procedure for total alkalies. Subtract the weight of the potassium sulfate (following section) from the weight of the total alkali sulfates and calculate the percentage of  $Na_2O$  from the difference.

$$\text{Per cent } Na_2O = \frac{\text{Wt. of alkali sulfates} - \text{wt. } K_2SO_4 \times 0.4364 \times 100}{\text{Wt. sample}}$$

*DETERMINATION OF POTASSIUM (K<sub>2</sub>O)*

*Procedure.*—Determine potassium as directed in the Rapid Method for potassium, beginning with paragraph three, using the water solution of the total alkali sulfates remaining from the preceding section.

*DETERMINATION OF CERIUM (CeO<sub>2</sub>)*

*Reagents.* 0.025 *N* Ferrous Ammonium Sulfate Standard Solution.—Weigh accurately 10 g. of pure  $Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$ . Dissolve in 200 ml. of water plus 10 ml. 1:1  $H_2SO_4$ . Dilute to one liter with water. Titrate with 0.025 *N*  $KMnO_4$  (to the first permanent pink color) 10 ml. portions of the ferrous ammonium sulfate plus 5 ml. of 1:1  $H_2SO_4$  in a 100-ml. volume.

$$CeO_2 \text{ titer} = \frac{\text{Ml. } KMnO_4 \times N_{KMnO_4} \times 0.1721}{\text{Ml. } Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O}$$

0.025 *N* Potassium Permanganate Standard Solution.—Weigh accurately 0.79 g. of  $KMnO_4$ . Prepare and standardize as directed on page 2233, using 50 mg. of primary standard sodium oxalate.

$$CeO_2 \text{ titer} = .N_{KMnO_4} \times 0.1721.$$

*Procedure.*—For glasses containing lead as a major constituent: weigh accurately a 1-g. ground sample into a platinum dish. Add 5 ml. of  $HNO_3$ , 15 ml. of  $HF$  and evaporate to dryness. Cover with a platinum lid, add 5 ml. of  $H_2SO_4$ , swirl the contents of the dish and warm the solution until the first fumes of sulfuric acid appear. Remove the cover and continue to fume lightly for two minutes. Cool, cover, add 10–20 ml. of water, transfer the solution and the precipitate to a 250-ml. beaker, dilute to about 100 ml. with hot water and boil the solution for 15 minutes. Let the precipitate settle for 10 minutes and filter through a coarse filter paper into a 500-ml. wide-mouth Erlenmeyer flask. Wash the precipitate with 50 ml. of a warm 2%  $H_2SO_4$  solution. Discard the precipitate. Add 4 ml. of 1:1  $H_2SO_4$  to the filtrate and heat to boiling.

(For glasses containing barium as a major constituent, proceed as follows:



To a 1 g sample in a platinum dish add 2 ml  $\text{HNO}_3$  3 ml  $\text{HClO}_4$  15 ml HF and evaporate to dryness. To the residue add 10 ml 1:1 HCl warm slightly transfer the solution to a 250 ml beaker dilute with water to about 100 ml and heat to boiling. Add several drops of methyl red indicator and  $\text{NH}_4\text{OH}$  dropwise until the solution becomes a distinct yellow then add 6–10 drops in excess. Boil for 1–2 minutes. Remove from the heat add 10 ml of 3% hydrogen peroxide and a small amount of paper pulp. Let stand until the precipitate settles filter through a coarse filter paper and wash several times with 1%  $\text{NH}_4\text{OH}$ . Discard the filtrate. Carefully dissolve the precipitate with 10–15 ml of hot 1:1 HCl and wash the paper thoroughly with hot water. Add 10 ml of 1:1  $\text{H}_2\text{SO}_4$  to the solution and heat until heavy fumes of  $\text{H}_2\text{SO}_4$  appear. Dilute to about 100 ml with water heat to boiling and proceed.)

Add 5 ml of a 0.25%  $\text{AgNO}_3$  solution and 5 g of ammonium persulfate dissolved in a small amount of water. The persulfate should be added slowly to the hot solution. Warm the solution for 5–10 minutes. Boil gently for 15 minutes to destroy the excess persulfate and cool rapidly in a cold water bath. Add 2–3 drops of 0.02%  $\text{V}$  ferroin indicator solution and titrate with standardized ferrous ammonium sulfate solution to a pure red-orange end point.

$$\text{Per cent CeO}_2 = \frac{\text{Ml Fe}(\text{NH}_4)_2(\text{SO}_4)_6 \cdot 6\text{H}_2\text{O} \times \text{CeO}_2 \text{ titer} \times 100}{\text{Wt sample}}$$

#### DETERMINATION OF TOTAL IRON ( $\text{Fe}_2\text{O}_3$ )

**Procedure**—Accurately weigh a ground sample which will contain no more than one mg of  $\text{Fe}_2\text{O}_3$  into a platinum dish. Add 5 ml  $\text{HNO}_3$  15 ml HF and evaporate to dryness. Cover add 5 ml of 1:1  $\text{H}_2\text{SO}_4$  heat until fumes of sulfuric acid appear remove the cover and fume lightly for 2–3 minutes. Cool add 20 ml of water and transfer the solution and precipitate to a 250 ml beaker. Dilute to about 80 ml with hot water boil for 15 minutes cool and filter through a fine filter paper. Wash the precipitate with water discard it and evaporate the filtrate to dryness.

To the residue add 5 ml of 1:1 HCl and 20 ml of hot water warm until the salts are in solution and transfer to a 250 ml volumetric flask. Proceed for the determination of iron as directed in the second paragraph of the procedure for Coloring Elements total iron.

#### DETERMINATION OF MANGANESE ( $\text{MnO}$ )

**Procedure**—Accurately weigh a ground sample which will contain no more than one mg of  $\text{MnO}$  into a platinum dish. Treat as directed in the first paragraph of the preceding section except that the filtrate is not evaporated to dryness. Complete the determination as directed in the second paragraph of the procedure for Coloring Elements manganese.

#### DETERMINATION OF TITANIUM ( $\text{TiO}_2$ )

**Procedure**—Accurately weigh a ground sample which will contain no more than one mg of  $\text{TiO}_2$  into a platinum dish. Add 5 ml  $\text{HNO}_3$  15 ml HF and evaporate to dryness. Cover add 10 ml of 1:1  $\text{H}_2\text{SO}_4$  heat until fumes of sulfuric acid appear remove the cover and fume lightly for 2–3 minutes. Cool add 20 ml of water and transfer the solution and precipitate to a 250 ml beaker. Dilute to about 80 ml with hot water boil for 15 minutes cool and filter through a fine

filter paper. Wash the precipitate with water. Transfer the filtrate to a 100-ml. volumetric flask and complete the determination as directed in the second paragraph of the procedure Coloring Elements, titanium.

#### DETERMINATION OF ZIRCONIUM ( $\text{ZrO}_2$ )

**Procedure.**—Mix the ignited precipitate of total  $\text{R}_2\text{O}_3$  (total  $\text{R}_2\text{O}_3$  in Lead Glass) with 5 g. of sodium bisulfate, cover the crucible and heat gently until a liquid fusion is obtained. Cool the melt, transfer to a 250-ml. beaker, add 40 ml. of 1:1  $\text{H}_2\text{SO}_4$ , 10 ml. of 3%  $\text{H}_2\text{O}_2$  and warm until dissolved. Dilute to approximately 200 ml. and add 2 g. of diammonium hydrogen phosphate. Keep the solution at 40–50°C. for several hours. (If only a little zirconium is present, remove from the heat and let stand overnight.) Filter through a coarse filter paper and wash thoroughly with a cold 5% solution of ammonium nitrate to remove the excess phosphate. Discard the filtrate. Place the paper and precipitate in a weighed platinum crucible. Char slowly until the carbon is gone and ignite to a constant weight in a muffle furnace at 1000°C. Cool in a desiccator and weigh as  $\text{ZrP}_2\text{O}_7$ .

$$\text{Per cent ZrO}_2 = \frac{\text{Wt. ZrP}_2\text{O}_7 \times 0.4647 \times 100}{\text{Wt. sample}}.$$

#### DETERMINATION OF ALUMINUM ( $\text{Al}_2\text{O}_3$ )

**Procedure.**—Subtract the sum of the percentages of  $\text{Fe}_2\text{O}_3$ ,  $\text{TiO}_2$ ,  $\text{ZrO}_2$ ,  $\text{MnO}$  and  $\text{CeO}_2$  from the percentage of total  $\text{R}_2\text{O}_3$  to obtain the percentage  $\text{Al}_2\text{O}_3$ .

#### DETERMINATION OF ARSENIC ( $\text{As}_2\text{O}_5$ )

**Procedure.**—Accurately weigh a 1-g. ground sample and treat as directed in the first paragraph of the section on the determination of total iron in lead glass.

To the residue, add 10 ml. of  $\text{HCl}$  and 20 ml. of water and warm until the salts are in solution. Dilute with water to 80 ml. and add 20 ml. of  $\text{HCl}$  to make the solution 30%  $\text{HCl}$  by volume. Finish the determination as directed in the regular procedure for arsenic, beginning with the addition of  $\text{H}_2\text{S}$  for 30 minutes.

#### DETERMINATION OF ANTIMONY ( $\text{Sb}_2\text{O}_5$ )

**Procedure.**—Determine antimony on the filtrate from the arsenic determination as directed in the regular procedure for antimony.

#### DETERMINATION OF CHLORIDE ( $\text{Cl}$ )

**Procedure.**—Determine as directed in the regular procedure for chloride.

#### DETERMINATION OF FLUORIDE ( $\text{F}$ )

**Procedure.**—Determine fluoride by the applicable procedure described in the "Determination of Fluoride" in borate glass below.

### THE ANALYSIS OF BORATE GLASSES

The following procedures are applicable to silicate glasses that contain boron, aluminum, titanium, zirconium, calcium, magnesium, sodium, potassium, barium and/or fluorine as major constituents and up to 2%  $\text{ZnO}$ , 0.5%  $\text{SO}_3$ , 0.5%  $\text{Cl}$ , 0.5%  $\text{Fe}_2\text{O}_3$ , 0.25%  $\text{As}_2\text{O}_5$  and 0.25%  $\text{Sb}_2\text{O}_5$ .

$R_2O_3$  group as before. Filter through a coarse filter paper and wash with hot 2% ammonium nitrate solution until free from chlorides. Combine the filtrates for the determination of  $ZnO$ . Place the paper and precipitate in a weighed platinum crucible. Heat until the carbon has been removed and ignite to a constant weight in a muffle furnace at  $950^\circ C$ . Cool in a desiccator and weigh as total  $R_2O_3$ . Save the ignited precipitate for the  $ZrO_2$  determination.

$$\text{Per cent } R_2O_3 = \frac{\text{Wt. } R_2O_3 \times 100}{\text{Wt. sample}}$$

#### DETERMINATION OF ZINC ( $ZnO$ )

*Procedure.*—Adjust the filtrate from the  $R_2O_3$  separation to 100 ml., add  $HCl$  dropwise until the red color of the indicator just appears, add  $NH_4OH$  until the solution becomes yellow, then add 2 ml. excess. Pass  $H_2S$  gas into the solution for twenty minutes, let stand overnight and filter onto a coarse filter paper that contains a small amount of paper pulp. Wash with a 10% ammonium hydroxide solution that has been saturated with  $H_2S$  gas. Save the filtrate for the determination of calcium. Place the paper and precipitate in a porcelain crucible, heat carefully until the carbon is destroyed and ignite to a constant weight in a muffle furnace at  $700^\circ C$ . Cool in a desiccator and weigh as  $ZnO$ .

$$\text{Per cent } ZnO = \frac{\text{Wt. } ZnO \times 100}{\text{Wt. sample}}$$

#### DETERMINATION OF ZIRCONIUM ( $ZrO_2$ )

*Procedure.*—Mix the  $R_2O_3$  precipitate with about 5 g. of sodium bisulfate and determine the zirconium as directed in the determination of zirconium in Lead Glass.

#### DETERMINATION OF CALCIUM OXIDE ( $CaO$ )

*Procedure.*—Acidify the filtrate from the zinc determination with  $HCl$  and add 5 ml. of bromine water. Boil to remove the  $H_2S$  and adjust the volume to about 125 ml. Complete the determination as directed in the fourth paragraph of the Regular Procedure for calcium.

#### DETERMINATION OF MAGNESIUM ( $MgO$ )

*Procedure.*—Determine the magnesium in the filtrate from the calcium determination as directed in the Regular Procedure for magnesium.

As an alternate to drying the magnesium hydroxyquinolate, filter the precipitate through a coarse filter paper, wash 10 times with 1:40  $NH_4OH$ , place in a weighed platinum crucible, char slowly and ignite to constant weight in a muffle furnace at  $1000^\circ C$ . Cool in a desiccator and weigh as  $MgO$ .

$$\text{Per cent } MgO = \frac{\text{Wt. } MgO \times 100}{\text{Wt. sample}}$$

NOTE.—Calcium and magnesium can be precipitated together when only small quantities are present as follows: Acidify the filtrate from the zinc determination (zinc in Borate Glass) with  $HCl$  and add 5 ml. of bromine water. Boil to remove the  $H_2S$ , adjust the volume to about 125 ml., heat to boiling and add 10 ml. of a saturated solution of ammonium oxalate and several drops of methyl red indicator. Add  $NH_4OH$  dropwise until the solution turns yellow, boil 5–10 minutes, let cool and add sufficient  $NH_4OH$  to make the

solution 5% by volume. Add 4 ml of a 5% 8 hydroxyquinoline solution. Heat to 60-70°C., stir and continue heating for 10-15 minutes. Do not boil. Let stand overnight. Filter the mixed precipitate through a fine filter paper, wash 10 times with 1:40  $\text{NH}_4\text{OH}$ , place in a weighed platinum crucible, char slowly and ignite to constant weight at 1000°C. Cool in a desiccator and weigh as  $\text{CaO}$  plus  $\text{MgO}$ .

$$\text{Per cent } (\text{CaO} + \text{MgO}) = \frac{\text{Wt } (\text{MgO} + \text{CaO}) \times 100}{\text{Wt sample}}$$

#### DETERMINATION OF TOTAL ALKALIES ( $\text{Na}_2\text{O} + \text{K}_2\text{O}$ )

*Procedure*—Determine the total alkalies as directed in the regular procedure for total alkalies.

#### DETERMINATION OF POTASSIUM ( $\text{K}_2\text{O}$ )

*Procedure*—Determine potassium on the water solution of the total alkali sulfates as directed in the rapid procedure for potassium, beginning with the third paragraph.

#### DETERMINATION OF ARSENIC ( $\text{As}_2\text{O}_3$ )

*Procedure*—Accurately weigh a 1 g ground sample into a platinum dish. Add 5 ml  $\text{HNO}_3$ , 15 ml  $\text{HF}$  and evaporate to dryness. To the residue, add 10 ml of  $\text{HCl}$  and 20 ml of water and warm until the salts are in solution. Dilute with water to 80 ml and add 20 ml of  $\text{HCl}$ . Finish the determination as directed in the regular procedure for arsenic, beginning with the addition of  $\text{H}_2\text{S}$  for 30 minutes.

#### DETERMINATION OF ANTIMONY ( $\text{Sb}_2\text{O}_3$ )

*Procedure*—Determine antimony on the filtrate from the arsenic determination as directed in the regular procedure for antimony.

#### DETERMINATION OF TOTAL IRON ( $\text{Fe}_2\text{O}_3$ )

*Procedure*.—Accurately weigh a ground sample which will contain no more than one mg of  $\text{Fe}_2\text{O}_3$  into a small platinum dish. Add 3 ml of 1:1  $\text{H}_2\text{SO}_4$ , 15 ml of  $\text{HF}$  and evaporate to fumes of sulfuric acid. Cool, add 20 ml of water, warm the solution, filter off any barium sulfate, wash with hot water and evaporate the filtrate to dryness. Cool, add 5 ml of 1:1  $\text{HCl}$  and 20 ml of hot water. Warm until the salts are in solution and transfer to a 250 ml volumetric flask. Complete the determination as directed in the second paragraph of the procedure for total iron in coloring elements.

#### DETERMINATION OF MANGANESE ( $\text{MnO}$ )

*Procedure*—Follow the procedure given under Coloring Elements, manganese.

#### DETERMINATION OF TITANIUM ( $\text{TiO}_2$ )

*Procedure*.—Follow the procedure given under Coloring Elements, titanium.

#### DETERMINATION OF ALUMINUM ( $\text{Al}_2\text{O}_3$ )

*Procedure*.—Subtract the sum of the percentages of  $\text{Fe}_2\text{O}_3$ ,  $\text{TiO}_2$ ,  $\text{ZrO}_2$ ,  $\text{MnO}$  and  $\text{ZnO}$  from the percentage of total  $\text{R}_2\text{O}_3$  to obtain the percentage of  $\text{Al}_2\text{O}_3$ .

DETERMINATION OF BORON ( $B_2O_3$ )

**Apparatus.** Distillation Apparatus.—Essentially the type described by Gwirtsman, Mavrodineanu and Coe.<sup>6</sup>

**pH Meter.**—Such as Leeds and Northrup No. 7664 equipped with a glass-saturated calomel electrode pair.

**Reagents.** Paranitrophenol Indicator.—Dissolve 1 g. of the reagent in 75 ml. of ethyl alcohol and dilute to 100 ml. with water.

**Phenolphthalein.**—Dissolve 1 g. of the reagent in 100 ml. of ethyl alcohol and dilute to 200 ml. with water.

**0.1 N Sodium Hydroxide Standard Solution.**—Weigh accurately and rapidly 4.0 g. of sodium hydroxide pellets. Dissolve and dilute to one liter with water. Store in a polyethylene bottle. Standardize against the 0.1 N boric acid standard solution as follows:

Measure from a pipet 25 ml. of the boric acid standard solution into a 250-ml. beaker, boil and cool under reduced pressure, dilute to 125 ml., stir with a magnetic stirrer and immerse the glass-calomel electrodes. Adjust to pH 5.4 with 0.1 N NaOH, add mannitol, and titrate to pH 8.5 with 0.1 N NaOH. Add enough mannitol to maintain a slight amount undissolved throughout the titration.

$$B_2O_3 \text{ titer} = \frac{\text{mg. } B_2O_3}{\text{ml. NaOH}}$$

**0.1 N Boric Acid Standard Solution.**—Fuse pure boric acid in a platinum dish. While still warm, crush the melt and transfer it to a weighing bottle. Accurately weigh 1.741 g. and dissolve in hot, recently boiled water. Cool and dilute to exactly 500 ml.

**Procedure.**—Accurately weigh a 0.5000-g. ground sample into a platinum crucible and mix with 3 g. of sodium carbonate. Cover the crucible and heat slowly over a Meker burner, gradually increasing the heat until a liquid fusion is obtained. Maintain this temperature for about 10 minutes. Cool and decompose the melt in the crucible in the minimum amount of HCl. After each addition of acid, swirl the mixture gently until the effervescence ceases. Thoroughly break up the solids with a stirring rod. Transfer to the sample chamber of the distillation apparatus with no more than 40 ml. of water and add approximately 1 g. of anhydrous calcium chloride for each ml. of solution.

Distill about 25 ml. of methyl alcohol into the sample flask before starting the distillation of the sample. Regulate the distillation of the sample to the minimum rate necessary to prevent further condensation of methyl alcohol in the sample flask. Collect two 100-ml. portions of distillate. Place the contents of the water trap in the second distillate. Immediately convert the methyl borate to sodium borate as follows: To each distillate portion add 3 drops of paranitrophenol and 10 drops of phenolphthalein. Add 0.5 N NaOH, first to the paranitrophenol end point, and then carefully to the phenolphthalein end point. Measure the volume of NaOH required between the two end points, then add twice this amount more. Transfer the solution to a glazed porcelain casserole and evaporate on a steam bath to approximately 25 ml. Both distillates are evaporated in the same casserole. Rinse the solution into a 250-ml. flask and add 1:5 HCl until the yellow color of the paranitrophenol just disappears. Heat to boiling and cool under reduced

<sup>6</sup> Gwirtsman, J., Mavrodineanu, R., and Coe, R. R., *Anal. Chem.*, **29**, 887, 1957.

pressure (attach to a vacuum line) Repeat this boiling and cooling to insure complete removal of  $\text{CO}_2$

Transfer the solution to a 250 ml beaker, dilute to 125 ml stir with a magnetic stirrer and immerse the glass-calomel electrode pair in the solution To neutralize the excess HCl adjust to pH 5.4 with 0.1 N NaOH added slowly Then add mannitol to the solution and titrate to a pH of 8.5 with 0.1 N NaOH standard solution Add enough mannitol to maintain a slight amount undissolved throughout the titration The NaOH equivalent to the  $\text{B}_2\text{O}_3$  is that required between pH 5.4 and 8.5

$$\text{Per cent B}_2\text{O}_3 = \frac{\text{ml NaOH} \times \text{B}_2\text{O}_3 \text{ titer} \times 100}{\text{Wt sample}}$$

#### DETERMINATION OF FLUORIDE (F)

**Apparatus**—A satisfactory type of distillation apparatus is described in the section on the determination of boron in Borite Glass

**Reagents** Chloroacetate Buffer—Dissolve 9.45 g of monochloroacetic acid and 2 g of sodium hydroxide pellets in 100 ml of water Store in a polyethylene bottle

**Fluoride Standard Solution (1 ml = 0.015 mg F)**—Accurately weigh 0.0332 g of pure dried sodium fluoride Dissolve in water and dilute to exactly one liter

**Fluoride Standard Solution, (1 ml = 1 mg F)**—Weigh accurately 2.210 g of pure dried sodium fluoride Dissolve and dilute to one liter with water Store in a polyethylene bottle

**0.1 N Thorium Nitrate Standard Solution**—Weigh accurately 13.8 g of  $\text{Th}(\text{NO}_3)_4 \cdot 4\text{H}_2\text{O}$  dissolve and dilute to one liter with water Store in a dark bottle Standardize as follows Pipet 10 ml of the fluoride standard solution (1 ml = 1 mg F) into a 250 ml beaker Dilute to 150 ml and follow the directions below beginning with the second paragraph of the titrimetric procedure

$$\text{F titer} = \frac{\text{Mg F}}{\text{ml Th}(\text{NO}_3)_4}$$

**Zirconyl Chloride**—Dissolve 0.263 g of zirconyl chloride octahydrate in 50 ml of water Add 700 ml of HCl and dilute to exactly one liter with water

**Absorption Spectrophotometric Procedure (0-10% F)** Preparation of the Standard Curve—Pipet 1, 2, 3, and 4 ml portions of the standard fluoride solution (1 ml = 0.015 mg F) into 100 ml volumetric flasks Dilute partially with water add with a pipet 5 ml of 0.18% eriochrome cyanine R solution and 5 ml of zirconyl chloride solution and complete the dilution with water Measure the absorbance at 526  $\text{m}\mu$  against a reference solution composed of 10 ml of 0.18% eriochrome cyanine R and 7 ml of HCl diluted to 200 ml with water Plot the absorbance against the mg of F

**Procedure**—Accurately weigh a 0.5 g ground sample into a platinum crucible Mix thoroughly with 3 g of  $\text{Na}_2\text{CO}_3$  Cover and fuse slowly over a Meker burner Cool transfer the melt to a 250 ml beaker add 75 ml of hot water and warm to disintegrate the melt

Filter through a coarse filter paper into a 250 ml volumetric flask Wash the residue 5 times with very hot water and discard Cool the filtrate and dilute to volume Pipet a 25 ml aliquot into the sample chamber of the distillation appa

ratus described in the section on the determination of boron in Borate Glass. Add approximately 0.2 g. of powdered  $\text{SiO}_2$  and 50 ml. of  $\text{HClO}_4$ .

Cool the condenser and begin heating the sample chamber and the steam generator (escape tube open). When the temperature in the chamber has reached  $130^\circ\text{C}$ ., direct the steam from the generator into the chamber by closing the escape tube. Maintain the temperature in the chamber at  $135\text{--}140^\circ\text{C}$ . during the distillation. Collect 250 ml. of distillate in a polyethylene bottle. Mix well and pipet a 50-ml. aliquot (should contain not more than 0.06 mg. of F) into a 100-ml. volumetric flask.

Add to the flask 5 ml. each of 0.18% eriochrome cyanine-R solution and zirconyl chloride solution, dilute to volume and read the absorbance at  $526\text{ m}\mu$  against the reference solution indicated above. Determine the concentration of F from the standard curve.

$$\text{Per cent F} = \frac{\text{Wt. F} \times 5000}{\text{Wt. sample}}$$

**Titrimetric Procedure (1–5% F).**—Accurately weigh a 0.5-g. ground sample into a platinum crucible. Treat the sample as directed in the first paragraph of the spectrophotometric procedure. Filter through a coarse filter paper into a 250-ml. beaker and wash the residue 5 times with very hot water. The volume of the filtrate should be about 150 ml.

Cool the solution, add 10 drops of 0.05% sodium alizarinsulfonate indicator solution and HCl until the pink color turns to pure yellow. Add 1 N NaOH until the pink color of the indicator just reappears, then 1:200 HCl until the pink just disappears. Adjust the pH between 2.9 and 3.2 by adding 3–5 ml. of chloroacetate buffer. Check the pH with pHYdrion paper. Titrate with 0.1 N  $\text{Th}(\text{NO}_3)_4$  solution to the appearance of the first permanent pink color.

$$\text{Per cent F} = \frac{\text{Ml. Th}(\text{NO}_3)_4 \times \text{F titer} \times 100}{\text{Wt. sample}}$$

**Gravimetric Procedure (>5% F).**—Prepare a 0.5-g. sample as directed in the first paragraph of the spectrophotometric procedure. Filter through a coarse filter paper into a 250-ml. beaker and wash the residue 5 times with hot water. Discard the residue. The volume of the filtrate should be about 150 ml. Heat to boiling and add slowly a suspension of zinc oxide (0.5 g.  $\text{ZnO}$  in 20 ml. of 1:20  $\text{HNO}_3$ ), boil for 1–2 minutes, let stand until cool, filter through a hardened coarse filter paper into a 400-ml. beaker and wash 5 times with hot water. Discard the precipitate. Adjust the volume of the filtrate to 250–300 ml. and add 3 drops of bromophenol blue indicator. Make the solution acidic with 1:1  $\text{HNO}_3$  and then just alkaline with 5% NaOH. Add 0.2 g. of NaCl, 1 ml. of HCl, 5 g. of lead nitrate and warm until the lead nitrate has dissolved. Immediately add 5 g. of sodium acetate trihydrate and stir vigorously. Warm for 30 minutes with occasional stirring, then let stand overnight at room temperature. Filter through a fine filter paper, wash the beaker and paper twice with iced water, then four times with a saturated solution of lead chlorofluoride and finally once more with iced water. Transfer the paper and precipitate to the precipitation beaker, add 100 ml. of 5:95  $\text{HNO}_3$  and boil until the precipitate has dissolved (requires about 5 minutes). Filter through a coarse filter paper and wash about 10 times with water. Bring the

filtrate to a boil and add a slight excess of a 1% solution of silver nitrate. Boil the solution for several minutes and let stand overnight in a dark place. Filter the precipitate into a Gooch filtering crucible that contains a glass fiber filter paper. Wash with cold 1.99  $\text{HNO}_3$  solution dry at  $110^\circ\text{C}$  for one hour, cool in a desiccator and weigh as  $\text{AgCl}$ .

$$\text{Per cent F} = \frac{\text{Wt AgCl} \times 0.1326 \times 100}{\text{Wt sample}}.$$



# THE ANALYSIS OF SILICATE ROCKS

The word "rocks" has been used as a broad compositional term in the title of this section. An attempt is made here to give methods for the analysis of the major types of naturally occurring silicates which are used as raw materials in manufacturing processes. The materials are listed in two compositional groups, namely: (1) quartz sands, and (2) clays and feldspars. The procedures given for the second group generally apply to the common igneous and metamorphic rocks and raw materials such as aplite, nephylene syenite, pyrophyllite, talc, high-alumina sands, and clays.

## THE ANALYSIS OF QUARTZ SANDS

The following procedures are applicable to sands which contain at least 96%  $\text{SiO}_2$  and no more than 2%  $\text{Al}_2\text{O}_3$ . High alumina sands (over 2%  $\text{Al}_2\text{O}_3$ ) should be analyzed as directed in The Analysis of Clays and Feldspars. For rapid or partial analysis, the procedures given in the section on Rapid Procedures are directly applicable to quartz sands. Since only small amounts of coloring oxides will be present normally in these sands, the procedures given in the section on Coloring Elements can be used. When analyzing quartz sands using the procedures written for glass analysis, the amounts of HF indicated in the procedures should be added in several small portions to avoid loss of sample due to too vigorous a reaction.

### DETERMINATION OF NON-VOLATILE RESIDUE

*Procedure.*—Accurately weigh 5 g. of sample (40 mesh) into a weighed 30-ml. platinum crucible. Add 1 ml. of 1:1  $\text{H}_2\text{SO}_4$  and 8 ml. of HF. Warm on a hot plate until the reaction begins. Remove from the hot plate, and add 5 ml. of HF to slow the reaction. Continue alternately to warm, cool and add HF to the solution as long as an active reaction occurs upon heating. When the danger of boiling over has passed, fill the crucible  $\frac{3}{4}$  full of HF, evaporate to dryness and expel the excess sulfuric acid. Ignite to a constant weight in a muffle furnace at 950–1000°C., cool in a desiccator and weigh. Save the residue for the determination of total  $\text{R}_2\text{O}_3$ .

$$\text{Per cent Non-Volatile} = \frac{\text{Wt. residue} \times 100}{\text{Wt. sample}}.$$

### DETERMINATION OF SILICON ( $\text{SiO}_2$ )

*Procedure.*—The percentage of total  $\text{SiO}_2$  is calculated by subtracting the percentage of non-volatile residue from 100.

### DETERMINATION OF TOTAL $\text{R}_2\text{O}_3$ ( $\text{Al}_2\text{O}_3$ , $\text{Fe}_2\text{O}_3$ , $\text{TiO}_2$ , $\text{ZrO}_2$ )

*Procedure.*—Add approximately 5 g. of sodium bisulfate to the residue in the crucible from section on Non-Volatile Residue, cover with a platinum lid and heat gently over a Meker burner until a clear liquid is obtained. Cool, transfer the melt to a 250-ml. beaker, rinse the lid and crucible, add 25 ml. of 1:1 HCl and

warm until the salts are in solution (If any barium is present, it will remain as insoluble  $\text{BaSO}_4$  and should be filtered off) Complete the determination as directed under the Regular Procedure for  $\text{R}_2\text{O}_3$ , beginning with the addition of 10 ml of bromine water Save the ignited precipitate for the determination of zirconium

#### DETERMINATION OF ZIRCONIUM ( $\text{ZrO}_2$ )

*Procedure.*—Determine the zirconium as directed in the section on the determination of Zirconium in Lead Glass

#### DETERMINATION OF ALUMINUM ( $\text{Al}_2\text{O}_3$ )

*Procedure*—Subtract the sum of the percentages of  $\text{Fe}_2\text{O}_3$  (page 2244)  $\text{TiO}_2$  (page 2246), and  $\text{ZrO}_2$  from the percentage of total  $\text{R}_2\text{O}_3$ . Alternately, weigh a 1.000 g ground sample into a platinum dish. Add several ml of water, 15 ml of HF (slowly) and 5 ml of  $\text{HClO}_4$ . Swirl gently to mix. With the platinum cover slightly displaced, heat until most of the hydrofluoric acid is evaporated. Remove the platinum cover and evaporate to dense fumes of perchloric acid. Cool, rinse the lid and sides of the dish with a small quantity of water and evaporate to dryness. To the residue in the dish, add 1 ml of HCl and 10 ml of water. Warm to dissolve the salts, cool, scrub the lid and dish with a rubber policeman and transfer the entire sample to a 250 ml beaker. Complete the determination as directed in the Rapid Procedure for aluminum, beginning with the second paragraph.

Per cent  $\text{Al}_2\text{O}_3$  =

$$\frac{\left[ (\text{ml EDTA} \times \text{Cu equiv}) - \left( \text{ml Cu} + \frac{\% \text{Fe}_2\text{O}_3 \times 0.01}{\text{Fe}_2\text{O}_3 \text{ titer}} \right) \right] \text{Al}_2\text{O}_3 \text{ titer} \times 100}{\text{Wt sample}}$$

#### DETERMINATION OF CALCIUM AND MAGNESIUM ( $\text{CaO}$ and $\text{MgO}$ )

*Procedure*—Weigh accurately a 2 g ground sample into a platinum dish. Add several ml of water, 10 ml of  $\text{HClO}_4$  and 25–30 ml of HF. Swirl gently to mix. Cover, evaporate to dense fumes of perchloric acid, cool, rinse the lid and sides of the dish with a small amount of water and evaporate to dryness. To the residue in the dish add 1 ml of HCl and 10 ml of water. Warm to dissolve the salts and cool. Scrub the lid and dish with a rubber policeman and transfer the contents to a 250 ml volumetric flask. Dilute to volume and mix thoroughly. Pipet two 100 ml aliquots into 250 ml beakers or Erlenmeyer flasks.

Determine either the sum ( $\text{CaO}$  plus  $\text{MgO}$ ) or the individual elements as directed under the Rapid Procedure for calcium and magnesium, beginning with the procedure for  $\text{CaO}$  titration or  $\text{CaO} + \text{MgO}$  titration.

#### DETERMINATION OF CALCIUM ( $\text{CaO}$ )—ALTERNATE PROCEDURE

*Procedure.*—For  $\text{CaO}$  contents up to 0.5%, a flame spectrophotometric method is useful. See following section for directions.

#### DETERMINATION OF SODIUM AND POTASSIUM ( $\text{Na}_2\text{O}$ and $\text{K}_2\text{O}$ )

*Reagents.* Calcium Standard Solution, (1 ml = 1 mg.  $\text{CaO}$ )—Dry the purest calcium carbonate available at  $110^\circ\text{C}$  for 3 hours and accurately weigh 1.7848 g

into a platinum dish. Cover the dish with a platinum lid and carefully add 25 ml. of 1:5  $\text{HClO}_4$ . Evaporate to fumes of perchloric acid. Rinse the lid and sides of the dish and evaporate to dryness. Dissolve the residue with water and dilute to exactly one liter.

**Potassium Standard Solution**, (1 ml. = 1 mg.  $\text{K}_2\text{O}$ ).—Dry the purest potassium chloride available at  $110^\circ\text{C}$ . for 2 hours, accurately weigh 1.5830 g., dissolve in water and dilute to exactly one liter.

**Sodium Standard Solution**, (1 ml. = 1 mg.  $\text{Na}_2\text{O}$ ).—Dry the purest sodium chloride available at  $110^\circ\text{C}$ . for 2 hours, accurately weigh 1.8860 g., dissolve in water and dilute to exactly one liter.

**Preparation of the Standard Curve**.—Prepare a series of standard solutions containing amounts of  $\text{Na}_2\text{O}$ ,  $\text{K}_2\text{O}$ , and/or  $\text{CaO}$  in each solution which approximate the quantities likely to occur in the sample by pipetting known quantities of the reagents above into a volumetric flask and diluting to one liter. This will minimize the effect of interferences between these elements.

Introduce the standard solutions into the flame spectrophotometer as directed by the manufacturer. Read the intensity of the emitted light at  $589\text{ m}\mu$  for sodium,  $767\text{ m}\mu$  for potassium and  $423\text{ m}\mu$  for calcium. Prepare three standard curves by plotting the measured intensities against the mg. of  $\text{Na}_2\text{O}$ ,  $\text{K}_2\text{O}$ , and  $\text{CaO}$ . Subtract the value of a blank carried through all steps of the determination.

**Procedure**.—Accurately weigh a 1-g. ground sample into a platinum dish. Add several ml. of water, 10 drops of  $\text{HClO}_4$  and 15 ml. of  $\text{HF}$ . Cover the dish and evaporate to dryness. Cool, rinse the lid and sides of the dish with water, add 10 drops of  $\text{HClO}_4$ , cover and evaporate again to dryness. Rinse the lid and sides of the dish with water, add 2 drops of  $\text{HClO}_4$  and evaporate to 5 ml. Then add a small amount of paper pulp.

Add one drop of methyl red indicator and precipitate the  $\text{R}_2\text{O}_3$  group by adding to the hot solution 1:9  $\text{NH}_4\text{OH}$  until the indicator turns to yellow, then add 4–5 drops in excess. Boil for about one minute to coagulate the precipitate, cool slightly and filter onto a coarse filter paper into a 25-ml. volumetric flask. Wash with a hot solution consisting of 1 ml. of  $\text{HClO}_4$  in 500 ml. of water neutralized with  $\text{NH}_4\text{OH}$  just to the yellow color of methyl red indicator. Add 1 *N*  $\text{HClO}_4$  to the solution in the flask until the red color of the indicator just appears. Cool, dilute to volume and transfer to a dry polyethylene bottle.

Introduce the sample into the flame spectrophotometer as directed by the manufacturer. Wear rubber gloves when handling samples to minimize contamination. Read the intensity of the emitted light at  $589\text{ m}\mu$  for sodium,  $767\text{ m}\mu$  for potassium, and  $423\text{ m}\mu$  for calcium. Determine the weights of  $\text{Na}_2\text{O}$ ,  $\text{K}_2\text{O}$ , and  $\text{CaO}$  from the standard curves. Subtract the value of a blank determination carried through all steps of the determination.

$$\text{Per cent Na}_2\text{O, K}_2\text{O, or CaO} = \frac{\text{Wt. oxide} \times 100}{\text{Wt. sample}}.$$

## THE ANALYSIS OF CLAYS AND FELDSPARS

The following procedures are applicable to silico-aluminates that contain calcium, magnesium, sodium and/or potassium as major constituents and not more than 5% each of barium, iron, titanium, and zirconium.

## DETERMINATION OF MOISTURE

*Procedure*—Accurately weigh a 1 g ground sample into a weighed platinum crucible. Dry the sample to constant weight (1–2 hours) in an oven at 105°C, cool in a desiccator and weigh.

$$\text{Per cent Moisture} = \frac{\text{Wt loss} \times 100}{\text{Wt sample}}$$

## DETERMINATION OF IGNITION LOSS

*Procedure*—Place the sample from the moisture determination in a muffle furnace, ignite to constant weight at 1000°C, cool in a desiccator and weigh.

$$\text{Per cent Ignition Loss} = \frac{\text{Wt loss} \times 100}{\text{Wt sample}}$$

DETERMINATION OF SILICON ( $\text{SiO}_2$ )

*Procedure*—Accurately weigh a 0.5 g ground sample into a 30 ml platinum crucible. Mix thoroughly with 6 g of sodium carbonate. Cover with a platinum lid and heat slowly, gradually increasing the heat until a liquid fusion is obtained. Maintain this temperature for 20–30 minutes. Remove the crucible from the heat and swirl the melt so that it coats in a thin shell on the inner crucible wall. Transfer the melt with hot water to a glazed porcelain casserole, rinse the crucible and lid with 1 l HCl, add 30 ml of 1 l HCl to the casserole and evaporate to dryness on a steam bath or a hot plate. Continue heating until the odor of HCl can no longer be detected. Add 30 ml of 1.3 HCl, heat for 10–15 minutes, filter onto a coarse filter paper and wash with hot water until free of chlorides. Place the filter paper and precipitate in an unweighed platinum crucible. Complete the determination as directed in the third paragraph of the Regular Procedure for silicon. Save the filtrate and the non siliceous residue in the crucible for the determination of total  $\text{R}_2\text{O}_3$ .

DETERMINATION OF TOTAL  $\text{R}_2\text{O}_3$  ( $\text{Al}_2\text{O}_3$ ,  $\text{Fe}_2\text{O}_3$ ,  $\text{TiO}_2$ ,  $\text{ZrO}$ )

*Procedure*—Fuse the residue that remains from the silica determination with about 1 g of sodium carbonate. Cool, dissolve the melt in a small amount of 1 l HCl and add to the silica filtrate. Evaporate the solution to about 125 ml, add 10 ml of bromine water, 10 grams of ammonium chloride and boil to volatilize the bromine. Add several drops of methyl red indicator and proceed as directed in the Regular Procedure for  $\text{R}_2\text{O}_3$ , beginning with the first addition of  $\text{NH}_4\text{OH}$ . Before the second precipitation, add 5 g of ammonium chloride to the acid solution of the first precipitate. The filtrates may be used for the determination of calcium and magnesium.

$$\text{Per cent } \text{R}_2\text{O}_3 = \frac{\text{Wt } \text{R}_2\text{O}_3 \times 100}{\text{Wt sample}}$$

DETERMINATION OF TOTAL IRON (as  $\text{Fe}_2\text{O}_3$ )

*Reagent* 0.025 N Potassium Permanganate—Weigh accurately 0.79 g of  $\text{KMnO}_4$ . Prepare and standardize as directed on page 2233, using 50 mg of primary standard sodium oxalate.

$$\text{Fe}_2\text{O}_3 \text{ titer} = N_{\text{KMnO}_4} \times 0.07985$$

*Procedure.*—Mix the ignited  $R_2O_3$  precipitate with 6–8 g. of sodium bisulfate (or potassium pyrosulfate), cover, heat over a Meker burner until a clear fusion is obtained. Cool, dissolve the melt in 10 ml. of 1:1  $H_2SO_4$  and 200 ml. of water. If only a low percentage of iron is present, determine as directed in the section on Coloring Elements. If not, heat the solution to boiling and pass in  $H_2S$  gas for 10–15 minutes to reduce the iron. Filter onto a coarse filter paper, wash several times with water made just acidic with  $H_2SO_4$  and saturated with  $H_2S$ . Again pass  $H_2S$  gas into the solution for 10 minutes. Pass  $CO_2$  into the solution and boil to expel the excess  $H_2S$ . Continue the flow of  $CO_2$  and cool the solution rapidly. Titrate the iron with 0.025  $N$   $KMnO_4$ . Save the solution for the determination of titanium.

$$\text{Per cent } Fe_2O_3 = \frac{\text{Ml. } KMnO_4 \times Fe_2O_3 \text{ titer} \times 100}{\text{Wt. sample}}$$

#### DETERMINATION OF TITANIUM ( $TiO_2$ )

*Procedure.*—Dilute to exactly 200 ml. the solution in which the iron was titrated and pipet an aliquot that will contain no more than one mg. of  $TiO_2$  into a 100-ml. volumetric flask. Add 5 ml. of  $H_2SO_4$ , 5 ml. of 3% hydrogen peroxide, and dilute to volume. Read the absorbance at 410  $m\mu$  against a reagent blank. Refer to section on Coloring Elements, titanium, concerning the preparation of the standard curve and the calculations.

#### DETERMINATION OF ZIRCONIUM ( $ZrO_2$ )

*Procedure.*—Combine the solutions from the preceding section (remainder of 200 ml., diluted aliquot, and solution in photometer cell). Add sufficient  $H_2SO_4$  to obtain a 10%  $H_2SO_4$  final concentration. Add 5 ml. of  $H_2O_2$  and 2 g. of di-ammonium hydrogen phosphate. Keep the solution at 40–50°C. for two hours or remove from the heat and let stand overnight. Filter onto a coarse filter paper and wash thoroughly with a cold 5% solution of ammonium nitrate. Discard the filtrate. Place the paper and precipitate in a weighed platinum crucible. Char slowly until the carbon is gone and ignite to a constant weight in a muffle furnace at 1000°C. Cool in a desiccator and weigh as  $ZrP_2O_7$ .

$$\text{Per cent } ZrO_2 = \frac{\text{Wt. } ZrP_2O_7 \times 0.4647 \times 100}{\text{Wt. sample}}$$

#### DETERMINATION OF ALUMINUM ( $Al_2O_3$ )

*Procedure.*—Subtract the sum of the percentages of  $Fe_2O_3$ ,  $TiO_2$ , and  $ZrO_2$  from the percentage of total  $R_2O_3$ .

#### DETERMINATION OF BARIUM ( $BaO$ )

*Procedure.*—Determine the barium as directed in the Regular Procedure for barium. Save the filtrate for the determination of calcium.

#### DETERMINATION OF CALCIUM ( $CaO$ )

*Procedure.*—Evaporate the filtrate from the barium determination to dryness. Add 15 ml. of 1:1  $HCl$ , 100 ml. of water, and warm to dissolve the soluble salts. Add 10 g. of ammonium chloride and determine the calcium as directed in the Regular Procedure for calcium, beginning with the third paragraph.

If it is desired to determine the calcium on the filtrate from the preceding section on total  $R_2O_3$  follow the procedure as directed in the Regular Procedure for calcium beginning with the fourth paragraph

**DETERMINATION OF MAGNESIUM ( $MgO$ )**

*Procedure*—Determine magnesium on the filtrate from the calcium determination as directed in the Regular Procedure for magnesium Save the filtrate for the determination of the total alkalis

**DETERMINATION OF TOTAL ALKALIES ( $Na_2O + K_2O$ )**

*Procedure*—Determine the total alkalis on the filtrate from the magnesium determination as directed in the Regular Procedure for total alkalis

**DETERMINATION OF POTASSIUM ( $K_2O$ )**

*Procedure*—Determine the potassium on a water solution of the total alkalis from the preceding section as directed in the Rapid Procedure for potassium beginning with the third paragraph

**DETERMINATION OF CHROMIUM ( $Cr_2O_3$ ) AND MANGANESE ( $MnO$ )**

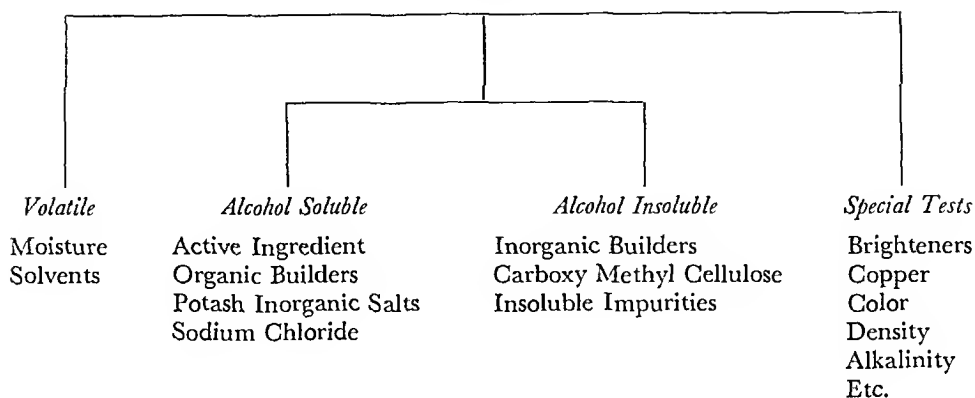
*Procedure*—When present in small quantities, determine as directed under Coloring Elements

## GENERAL SCHEME OF ANALYSIS

A general scheme of analysis is shown diagrammatically here.

## General Method of Analysis

## Sample



## SAMPLING

Sampling Methods conform generally to the procedures of the American Society for Testing and Materials. For more complete details, reference should be made to ASTM Methods D460-58 and D1570-58T.

**Powders and Flakes Packed in Cans or Cartons.**—One can or carton shall be taken at random from not less than 1% of the shipping containers, provided each package contains not less than 50 lb. (22.7 kg.). In the case of smaller containers, a can or carton shall be taken at random from each lot of containers totaling not more than 5000 lb. (2268 kg.) or fraction thereof. The gross sample shall in all cases consist of not less than three cans or cartons taken at random from separate containers. In the case of very large lots where the sample drawn as above will amount to more than 20 lb. (9.1 kg.), the percentage of packages sampled shall be reduced so that the amount drawn will not exceed 20 lb. (9.1 kg.). The individual cans or cartons shall be tightly wrapped at once in paraffined paper and sealed by rubbing the edges with a heated iron. The wrapped cans or cartons shall be placed in an airtight container, which should be nearly filled, and which shall then be sealed, marked, and sent to the laboratory for test. Samples shall be kept cool until tested.

**Powders and Flakes in Bulk.**—A grab sample of not less than 0.5 lb. (227 g.) shall be taken at random from not less than 1% of the shipping containers, provided each package contains not less than 100 lb. (45.4 kg.). In the case of smaller containers, a grab sample of not less than 0.5 lb. (227 g.) shall be taken at random from each lot of containers totaling not more than 10,000 lb. (4536 kg.) or fraction thereof. The gross sample shall in all cases consist of not less than three grab samples of 0.5 lb. (227 g.) each taken at random from separate containers. In the case of very large lots where the sample drawn as above will amount to more than 20 lb. (9.1 kg.), the percentage of packages sampled shall be reduced so that the

amount drawn shall not exceed 20 lb (9.1 kg). The sampler shall rapidly mix the gross sample and place it in an airtight container which shall be filled, sealed, marked, accurately weighed with its weight and the date of weighing recorded on the package and be sent to the laboratory for test. Samples shall be kept cool until tested.

**Liquids**—A sample of not less than 0.5 pt (236.6 ml) shall be taken at random from not less than 1% of the shipping containers provided each package contains not less than 10 gal (37.9 liters). In the case of smaller containers a sample of not less than 0.5 pt (236.6 ml) shall be taken at random from each lot of containers totaling not more than 1000 gal (3785.4 liters) or fraction thereof. The gross sample shall in all cases consist of not less than three samples of 0.5 pt (236.6 ml) each taken at random from separate containers. Before drawing the sample from the container selected the contents of the container shall be thoroughly agitated. The sampler shall thoroughly mix the gross sample, place it in clean dry cans or bottles which shall be completely filled and securely stoppered with clean corks or caps then sealed, marked, and sent to the laboratory for test.

**Pastes** **Pastes Packed in Cans or Cartons of 5 lb (2.27 kg) or Less**—One can or carton shall be taken at random from not less than 1% of the shipping containers provided each package contains not less than 50 lb (22.7 kg). In the case of smaller containers a can or carton shall be taken at random from each lot of containers totaling not more than 5000 lb (2268 kg) or fraction thereof. The gross sample shall in all cases consist of not less than three cans or cartons taken at random from separate containers. In the case of very large lots where the sample drawn as above will amount to more than 20 lb (9.1 kg) the percentage of packages sampled shall be reduced so that the amount drawn shall not exceed 20 lb (9.1 kg). The samples shall be wrapped, sealed, marked, and sent to the laboratory for test.

**Pastes Packed in Bulk**—A **trier sample** (see NOTE) of not less than 0.5 lb (227 g) shall be taken at random from not less than 1% of the shipping containers provided each package contains not less than 50 lb (22.7 kg). In the case of smaller containers a trier sample of not less than 0.5 lb (227 g) shall be taken at random from each lot of containers totaling not more than 5000 lb (2268 kg) or fraction thereof. The gross sample shall in all cases consist of not less than three 0.5 lb (227 g) samples each taken at random from separate containers. With very large lots where the sample drawn as above will amount to more than 10 lb (4.5 kg) the percentage of packages sampled shall be reduced so that the amount drawn shall not exceed 10 lb (4.5 kg). The sampler shall promptly place the gross sample in a clean dry airtight and watertight container which shall be filled, sealed, marked, and sent to the laboratory for test.

**NOTE**—A trier sample is obtained by inserting a trier into the material. A trier is a half round steel cylinder  $\frac{1}{2}$  to  $\frac{3}{4}$  inch in diameter, 6 to 36 inches in length, pointed on one end and having a grip handle on the other end. After insertion the trier is turned two or three times and upon removal a core of the material being sampled is obtained.

**Preparation of Sample** **Powders and Flakes**—Minimizing exposure to air rapidly disintegrate and mix the sample of powdered flake or chip product. If desired quarter down to about 1 lb (453.6 g). Weigh at once all portions for analysis preserving the remainder in an airtight container in a cool place.



**Liquids.**—No preparation of the sample of liquid, other than a thorough mixing, is necessary unless it is received during very cold weather, when it should be allowed to stand at least 1 hour after it has warmed to room temperature (20° to 30°C.) before it is tested, particularly for its lathering qualities (see NOTE).

**Pastes.**—Store preferably in glass. If crystals separate, melt on water bath (see NOTE).

**NOTE.**—If pastes or liquids are known to be acidic, and decomposition of sample can result from heating, the samples shall be adequately labeled for precautionary treatment and warmed to room temperature or other maximum temperature as agreed upon for mixing and sampling.

## METHODS OF ANALYSIS

In compiling these methods, the Standard Methods of the American Oil Chemists' Society and American Society for Testing and Materials have been used extensively and acknowledgment is hereby given. In some cases, the methods are not reproduced as standards, but have been found useful in the detergent industry.

**Purity of Reagents.**—Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available.<sup>1</sup> Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

Unless otherwise indicated, references to water shall be understood to mean reagent water conforming to the Specifications for Reagent Water (ASTM Designation D1193).<sup>2</sup>

**Other Reagents and Apparatus.**—Special reagents and apparatus will be shown in the individual methods where it is believed necessary for a complete understanding of the particular method.

## ALCOHOL-SOLUBLE MATERIAL

**Reagents.** **Ethyl Alcohol (95%).**—Ethyl alcohol conforming to Formula No. 30 or 3A of the U. S. Bureau of Internal Revenue. The alcohol should not be neutralized. Redistilled alcohol must be used if alkali absorption is more than 0.2 ml.

**Ethyl Alcohol (Absolute).**—Freshly boiled absolute ethyl alcohol conforming to either Formula No. 30 or 3A of the U. S. Bureau of Internal Revenue.

**Procedure.**—For pastes or liquids, weigh approximately 20 g. to the nearest 1 mg. and wash into a 400-ml. anti-bump beaker with ethyl alcohol (absolute). For powders, weigh 10 g. to the nearest 1 mg. and transfer to a 400-ml. anti-bump beaker.

Add 300 to 350 ml. of hot absolute ethyl alcohol. Cover with a watch glass and heat on the steam bath for at least 2 hours, stirring frequently to disperse solids and break up lumps. Have ready either a tared, 15-cm., rapid filter paper that

<sup>1</sup> Reagent Chemicals, American Chemical Society Specifications, Am. Chem. Soc., Washington, D. C. For suggestions on the testing of reagents not listed by the American Chemical Society, see Reagent Chemicals and Standards, by Joseph Rosin, D. Van Nostrand Co., Inc., Princeton, N. J., and the United States Pharmacopoeia.

<sup>2</sup> Book of ASTM Standards, Part 10, p. 1132, 1958.

has been dried in an open tin ointment box at  $105 \pm 2^\circ\text{C}$  for 1 hour cooled in a desiccator and weighed in the covered box or a tared Gooch or sintered glass crucible

At the end of 2 hours remove the beaker from the bath and decant the alcohol solution rapidly through the weighed filter paper or tared Gooch or sintered glass crucible retaining as much as possible of the residue in the beaker. Add 50 ml of hot ethyl alcohol (95%) to the residue in the beaker. Heat to boiling on a hot plate breaking up any lumps of the residue. Again decant the alcohol through the tared filter as before. Repeat again with another 50 ml portion of hot alcohol (95%).

Evaporate the residual alcohol from the residue in the beaker on the steam bath stirring at intervals especially near the end. Dissolve the residue in the beaker with 10 ml of hot water heating on the steam bath until solution is effected. Dilute the water solution with 200 ml of hot ethyl alcohol (absolute) bring to a boil on the steam bath and filter through the original filter paper. Finally transfer the precipitate to the paper with the aid of hot alcohol (absolute) and a policeman.

Wash the residue with hot ethyl alcohol (95%). Three or four washings will be required. Combine the filtrate and washings in a 1 liter volumetric flask cool make up to volume with alcohol (95%) and mix thoroughly.

Transfer a 200 ml aliquot to a tared Soxhlet flask. Evaporate on the steam bath in a gentle stream of clean dry oil free air until the residue has no odor of alcohol. Swirl the flask to bring the residue onto the sides of the flask to aid the escape of moisture. Dry 2 hours in the oven at  $90^\circ\text{C}$ . Cool in a desiccator and weigh. Break up residue with a glass rod. Return to the oven for 0.5 hour cool and reweigh. Repeat until constant weight is obtained.

**Calculations**—Calculate the uncorrected percentage of alcohol soluble matter as follows

$$\text{Alcohol soluble matter (uncorrected), per cent} = \frac{A}{B} \times 100$$

where  $A$  = grams of residue and

$B$  = grams of sample represented by the aliquot used

### ALCOHOL INSOLUBLE MATERIAL

**Procedure**—Place the filter paper containing the residue from the alcohol soluble matter in the ointment box (a tared sintered glass crucible may be used) and dry 2 hours or longer at  $105^\circ \pm 2^\circ\text{C}$  to constant weight. Cool in the desiccator and weigh.

### MOISTURE AND VOLATILE MATERIAL (OVEN METHOD)

**Procedure**—Weigh a  $5 \pm 0.1$  g sample rapidly in a tared 4-ounce aluminum dish tinned ointment box or glass dish. Dry to constant weight in an oven at  $150^\circ \pm 2^\circ\text{C}$ . Usually 45 minutes to 1 hour is sufficient. Soaps containing naphtha or as much as 1% glycerine give results too high on account of volatilization of these materials. Soaps containing silicate give results which are too low because some water is retained by the silicate. In these cases moisture should also be reported by difference after all other constituents have been determined.

Some soaps will char at  $150^\circ\text{C}$  but may be dried satisfactorily at  $105^\circ\text{C}$  usually two hours are sufficient. Soaps from linseed and other oxidizing oils absorb oxygen

and, if the oven is used, may gain in weight near the end of the test. For soaps from such oils or those containing naphtha and glycerine, the distillation method is much more satisfactory than any oven method.

### MOISTURE BY DISTILLATION

**Apparatus.**—The apparatus shall consist of a glass flask heated by suitable means and provided with a reflux condenser discharging into a trap and connected to the flask. The connections between the trap and the condenser and flask shall be interchangeable ground joints. The trap serves to collect and measure the condensed water and to return the solvent to the flask.

**Flask.**—A 1000-ml. flask of either the short-neck, round-bottom type or the Erlenmeyer type shall be used.

**Heat Source.**—The source of heat may be either an oil bath (stearic acid, paraffin wax, etc.), or an electric heater provided with a sliding rheostat or other means of heat control.

**Condenser.**—A water-cooled glass reflux condenser (see ASTM D1570-58T), having a jacket approximately 400 mm. (15¾ in.) in length, with an inner tube 9.5 to 12.7 mm. (⅜ to ½ in.) in outside diameter, and not less than 6.35 mm. (¼ in.) inside diameter, shall be used. The end of the condenser to be inserted in the trap may be ground off at an angle of 30° from the vertical axis of the condenser. When inserted into the trap, the tip of the condenser shall be about 7 mm. (¼ in.) above the surface of the liquid in the trap after the distillation conditions have been established.

**Trap.**—For greatest accuracy several trap sizes are allowable, depending upon the percentage of moisture expected:

<i>Moisture Expected, %</i>	<i>Size of Trap, ml.</i>
0 to 5, incl.....	5
Over 5 to 17, incl.....	10
Over 17 to 30, incl.....	10
Over 30 to 50, incl.....	25
Over 50 to 70, incl.....	25
Over 70 to 85, incl.....	25

Traps made of well-annealed glass graduated to contain one of the following specified volumes at 20°C. shall be used.

**5-ml. Trap.**—Subdivided into 0.1-ml. divisions with each 1 ml. line numbered (5 ml. at top). The error in any indicated capacity may not be greater than 0.05 ml.

**10-ml. Trap.**—Subdivided from 0 to 1 ml. in 0.1-ml. divisions and from 1 to 10 ml. in 0.2-ml. divisions.

**25-ml. Trap.**—Subdivided from 0 to 1 ml. in 0.1-ml. divisions and from 1 to 25 ml. in 0.2 ml. divisions.

**NOTE.**—The condenser and trap should be thoroughly cleaned before use.

**Solvent.** Xylene (or Toluene).—Saturate xylene (or toluene) with water by shaking with a small quantity of water and distill. Use the distillate for the determination.

**Procedure.**—Transfer to the 100-ml. flask, equipped with the proper size of trap, an amount of sample according to the percentage of moisture expected, as follows:

<i>Moisture Expected, %</i>	<i>Weight of Sample to be Used, g *</i>
0 to 5, incl	50 $\pm$ 5
Over 5 to 17, incl	50 $\pm$ 5
Over 17 to 30, incl	40 $\pm$ 4
Over 30 to 50, incl	30 $\pm$ 3
Over 50 to 70, incl	30 $\pm$ 3
Over 70 to 85, incl	25 $\pm$ 2

\* Weighed to the nearest 0.25 g

Add immediately about 100 ml of xylene or toluene. Place a small thin sheet of long fiber chemical resistant glass wool on the surface of the toluene (Pyrex and Kimax glass have been found satisfactory for this purpose). The glass wool should be thoroughly dried in the oven and held in the desiccator before use.

Connect the flask and receiver to the condenser and pour sufficient xylene or toluene down the condenser tube to cause a slight overflow through the side tube. Wrap the flask and tube leading to the receiver with asbestos cloth so that refluxing will be under better control.

Heat the oil bath with a gas burner or other source of heat or apply heat directly to the flask with an electric heater and distill slowly. The rate at the start should be approximately 100 drops per minute. When the greater part of the water has distilled over increase the distillation rate to 200 drops per minute until no more water is collected. Purge the reflux condenser during the distillation with 5 ml portions of xylene (or toluene) to wash down any moisture adhering to the walls of the condenser. The water in the receiver may be made to separate from the xylene (or toluene) by using a spiral copper or Nichrome wire. Move the wire up and down in the condenser occasionally thus causing the water to settle at the bottom of the receiver. Reflux for at least 2 hours and shut off the heat at the end of this period.

Wash down condenser with 1 ml of absolute ethanol ( $\text{CH}_3\text{CH}_2\text{OH}$ ). Adjust the temperature of the distillate to 20°C and read the volume of water.

*Comments on Above Methods*—Usually the sum of the alcohol soluble material alcohol insoluble material and volatile matter will add to 100%. When this does not occur decomposition of the sample during analysis should be suspected. When organic solvents are present moisture by distillation will differ from volatile material determined by oven drying. These volatile materials may be determined by a distillation procedure which follows.

### VOLATILE SOLVENTS

*Apparatus* Glass Distillation Apparatus, constructed in accordance with the specifications shown in the illustration Fig. 45.1

Flask, 500 ml short neck round bottom type

Water Cooled Condenser

Traps for solvents heavier than water constructed of well annealed glass and graduated to contain 5 ml at 20°C. It shall be subdivided into 0.1 ml divisions with each 1 ml line numbered and the 5 ml line at the top. The error at any indicated capacity shall not exceed 0.05 ml.

Calibrate the receiver by the following procedure: add ca 1 g of distilled water to a mixture of 80 g of xylene and 10 g of oleic acid. Conduct the distillation as

described in A.O.C.S. Official Method F 1a-44. Calibrate the receiver up to its maximum capacity at intervals of 1 ml.

Traps for solvents lighter than water constructed of well-annealed glass and graduated to contain 5 ml. at 20°C. It shall be subdivided into 0.1-ml. divisions

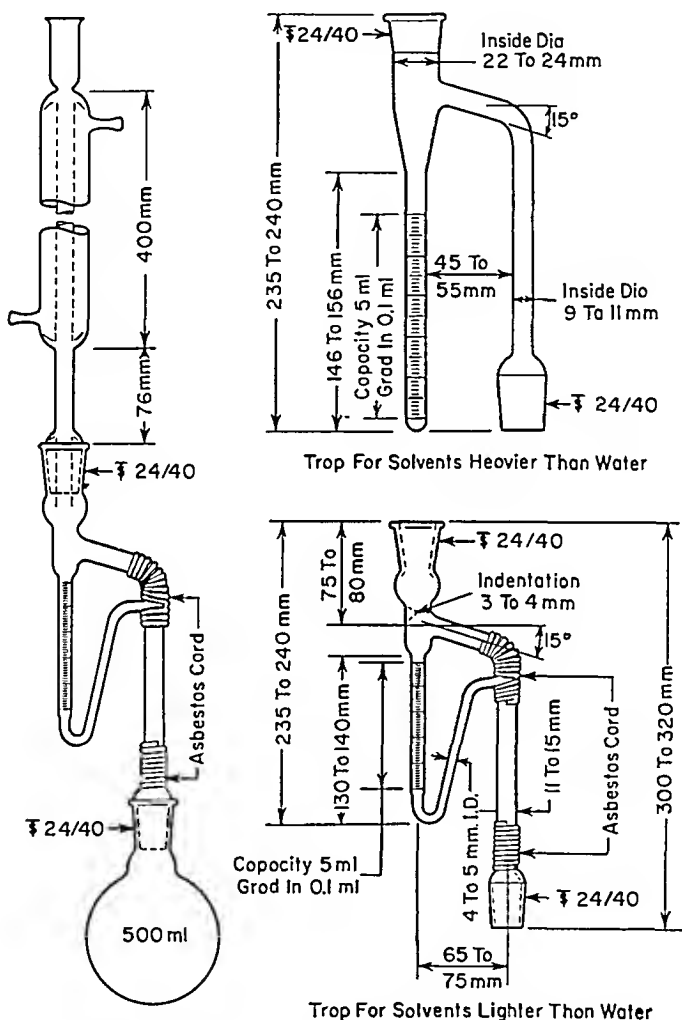


FIG. 45-1. Apparatus for Water-Immiscible Organic Solvents.

with each 1-ml. line numbered and the 5-ml. line at the top. The error at any indicated capacity shall not exceed 0.05 ml.

Calibrate the receiver by the following procedure: Insert a one-hole stopper containing a short piece of glass tubing into the lower opening of the trap. Attach a separatory funnel to the glass tube by means of rubber tubing. Fill the funnel with dichloroethyl ether or some other liquid heavier than and nonmiscible with water, open the stopcock and raise the funnel carefully until the liquid flows into

the receiver to approximately the 0.3 ml mark. Introduce exactly 1 ml of water with a pipet into the graduated arm followed by a drop of pine oil to protect the surface from evaporation. Measure the volume of the water in the tube. Raise the level of the solvent in the graduated tube *ca* 1 ml by raising the funnel and again read the volume in the graduated tube. Continue in this manner until the entire tube has been calibrated.

**Heat Source**, either an oil bath such as stearic acid or paraffin wax or an electric heater provided with a suitable means of control.

**Glass Beads or Pumice Stone.**

**Procedure**—Introduce *ca* 50 ml of distilled water into the distillation flask and a sufficient amount of the sample to yield *ca* 4 ml of solvent. This is conveniently done with a weighing bottle.

In the case of highly volatile solvents, it is preferable to remove the top of the weighing bottle and to drop the bottle and contents into the distillation flask.

If cresylic acid is present, the size of sample should be such as to yield *ca* 2.5 ml of solvent and add *ca* 1.5 ml of pine oil, exactly weighed to the distillation flask to reduce the gravity of the distillate.

Neutralize the solution rapidly with alkali *ca* 1 N, until slightly alkaline to phenolphthalein—the latter preferably added as powder. Add 2 g of  $\text{Na}_2\text{CO}_3$  and enough  $\text{CaCl}_2$  to prevent foaming (usually 3 to 5 g) and some glass beads and pumice stones to prevent bumping.

Attach the receiver to the condenser and fill the receiver with water by pouring through the condenser. Immediately attach the distillation flask and begin the distillation.

Heat at such a rate that the refluxing will start 7 to 10 minutes after the heat is applied, the water being at room temperature initially. Read the volume of solvent collected in the receiver 2 hours after refluxing starts and every hour thereafter until the test is complete. The test is complete when the volume of solvent increases by not more than 0.1 ml in any two consecutive hour periods. The source of heat is removed from the distillation flask and the latter cooled for exactly 3 minutes before taking readings.

The distillation is continued for an additional 15 to 30 minutes with the water in the condenser tube emptied as an additional precaution.

After completion of the test, allow to stand for at least 40 minutes in order to cool to approximately room temperature and to allow the distillate to settle clearly and then read the volume of solvent.

Remove *ca* 2.5 ml of solvent from the receiver with a pipet and determine the specific gravity in a 2 ml pycnometer. In the case of solvents heavier than water the former is separated by means of a small separatory funnel.

**Calculation**—

Water-immiscible organic solvents, %

$$= \frac{(\text{Weight of solvent} - \text{weight of pine oil, if present}) \times 100}{\text{Weight of sample}}$$

**NOTES**—In the presence of water miscible solvents (such as alcohol) that are also miscible with the water immiscible solvents some of the former will be found in the solvent layer. When there is an appreciable difference in the boiling points and gravities of the two types of solvents they may be separated qualitatively by a fractional distillation and the gravities of the fractions determined, from which together with the gravity of the solvent layer the amount of water immiscible solvents may be calculated.

In the case of pine oil or cresylic acid mixed with alcohol, the latter may be volatilized by heating over a hot plate with constant stirring to a temperature of *ca* 150°C., after which the gravity of the residue is determined. The quantity of the water-immiscible solvent may now be calculated as in the previous procedure. This method may be applied to all such mixtures where there is a considerable difference in boiling points and gravities and the gravity of one of the solvents is known.

When there is a difference in the gravities but not in the boiling points and the gravity of the water-miscible solvents is known, the water-immiscible solvent is extracted with ether over water, the ether evaporated, and the gravity of the residue determined. In this procedure it is assumed that the boiling point of the water-immiscible solvent is considerably higher than that of ether. In all other cases, to obtain the water-immiscible solvent it will be necessary to resort to a quantitative fractional distillation or to chemical means.

With samples yielding distillates that are both heavier and lighter than water, the distillation is first made with the trap for solvents heavier than water and, after flushing all the solvent floating on top of the water layer back into distillation flask and substituting the trap for solvents lighter than water, the distillation is continued to completion.

## METHODS FOR ACTIVE INGREDIENT AND OTHER ALCOHOL-SOLUBLE MATERIAL

The alcohol-soluble material in most detergents will contain, as indicated in the general analytical scheme, the active ingredient such as soap or synthetic, organic builders, sodium chloride, potash inorganic salts, and other organic materials which are present as impurities or by-products of the preparation or synthesis of the active ingredient. The type or types of active ingredients should be determined qualitatively before any analysis is started. This is best accomplished by means of infrared analysis which will not be described here for lack of space. Any good text on infrared analysis may be consulted.

If infrared equipment is not available, two simple tests can be conducted. Dissolve a portion of the alcohol-soluble material in water and acidify. If the active ingredient is a fatty acid salt (soap) the solution will no longer form suds and fatty acids will separate; if the active is not soap, sudsing will continue and no fatty material will separate. If both soap and synthetics are present, sudsing will continue and fatty acid will also separate. If non-soap active is present, it can be identified as anionic, cationic or non-ionic by titration with either a cationic or anionic solution using methylene blue in chloroform as an indicator. This method which follows can be interpreted in this way: if an anionic (other than soap), it will be titrated by a cationic solution, if cationic in nature, it can be titrated by the anionic solution and if non-ionic, it will not be titrated by either the anionic or cationic reagent.

## ACTIVE INGREDIENT AND EQUIVALENT COMBINED $\text{SO}_3^3$

This method is based on the fact that when equivalent amounts of a cationic and anionic detergent are present in a two-phase mixture of water and chloroform, methylene blue will color the two phases to the same degree. Sodium alkyl benzene sulfonate and sodium alkyl sulfate or other anionic detergent, either separately or in mixtures, can be titrated with a standard solution of cetyl trimethyl ammonium bromide. Likewise cetyl trimethyl ammonium bromide or other cationic material can be titrated by sodium alkyl benzene sulfonate. The titration is calculated to

<sup>3</sup> Barr, Oliver & Stubbings, JSCI, 67, Feb. 1948, p. 45. S. R. Epton, Trans. Farad. Soc., Vol. XLIV, Part 4, April, 1948, p. 226.

combined  $\text{SO}_3$ . The ultimate standard for the determination is alkyl benzene sulfonate or alkyl sulfate in which combined  $\text{SO}_3$  content has been carefully determined by the Parr bomb method and other analyses. Disulfonated alkyl benzene is not titrated.

**Interferences**—Large amounts of sodium chloride destroy the sensitivity of the end point and should be avoided. The method will not work in the presence of sodium iodide or ammonium thiocyanate.

**Reagents** **Anionic Detergent**—Alkyl benzene sulfonate or alkyl sulfate. Obtain as standard an alkyl benzene sulfonate or alkyl sulfate of known combined  $\text{SO}_3$  or active content.

**Cationic Detergent**—Cetyl trimethyl ammonium bromide (Eastman Tech No T6600). This reagent is known as Cetab. *Caution!* In solid form or in concentrated solution quaternary ammonium halides are irritating to the skin and mucous membranes though in the dilute solution employed in this method Cetab is not harmful.

**Chloroform**—A.C.S. Spec.

**Methylene Blue Indicator**—Dissolve 0.1 g methylene blue (Eastman P 573 or equivalent) in 100 ml distilled water. Transfer 30 ml of this solution to a 1 liter volumetric flask. Add 500 ml distilled water, 6.8 ml concentrated sulfuric acid, 50 g  $\text{NaH}_2\text{PO}_4 \cdot \text{H}_2\text{O}$  and shake until solution is complete. Dilute to the 1 liter mark and mix thoroughly.

**Apparatus** **Viewing Cabinet**—Metal 6 x 7 x 12" with special color interior. Constructed so the cylinder is viewed at about a  $75^\circ$  angle in order to eliminate reflected highlights.

**Burets (2)**—One for anionic and 1 or more for cationic detergent solution. These are preferably 25 ml burets connected to a reservoir. Burets with gravity feed give less trouble with foam on the meniscus. (J 697 from Scientific Glass Apparatus Co. is an example.)

**Beakers**—As necessary.

**Titration Vessel**—Pyrex glass test tube 25 x 300 mm with S 24/40 outer joint. Similar to catalog No M 35 900 (H. S. Martin & Co. 1916 Greenleaf Street, Easton, Ill.) except longer. Special order required.

**Glass Stopper**—Full length S 24/40 hollow penny head. Catalog No M 31 000 (H. S. Martin & Co.)

**Volumetric Flasks**—As necessary.

**Weighing Bottle**—For liquids (especially those readily volatile) a weighing bottle and catchweight should be used.

**Pipet**—10 ml calibrated.

**Graduated Cylinders**—10 ml, 25 ml.

**Preparation of Anionic and Cationic Solutions** **Solution 1**—Weigh  $1.5 \pm 0.001$  g of cetyl trimethyl ammonium bromide into a 250 ml beaker, add 100 ml of distilled water and stir until dissolved. Transfer quantitatively to a 1 liter volumetric flask and make to volume. Mix thoroughly. Standardize against Solution 2 following the procedure given for the sample under Operation.

$$N \text{ of solution 1} = \frac{\text{Ml of solution 2} \times N \text{ of solution 2}}{\text{Ml of solution 1}}$$

**Solution 2**—Weigh to  $\pm 0.001$  g a sample of standard alkyl benzene sulfonate or alkyl sulfate of a size to give exactly 0.320 g of combined  $\text{SO}_3$  into a 250 ml beaker. Dissolve in 100 to 200 ml warm distilled water. Transfer quantitatively



to a 1-liter volumetric flask and make to volume with distilled water at room temperature. Mix thoroughly. This is the primary standard against which Solution 1 is standardized. Solution 2 is 0.004 *N* in  $\text{SO}_3$ .

Solution 1 should be checked against Solution 2 at least weekly and Solution 2 should be renewed monthly.

**Procedure.**—Weigh accurately a sample of sufficient size to give approximately 0.320 g. of combined  $\text{SO}_3$  into a 250-ml. beaker. Sample size is critical. (See NOTES.) (Grams sample = 32/%  $\text{SO}_3$  expected.) Use about 700–800 ml. warm, distilled water to transfer quantitatively to a 1-liter volumetric flask. Warm on steam bath and shake gently until sample is dissolved and solution is clear. Cool, dilute to mark with distilled water and mix thoroughly.

Pipet 10.0 ml. of the sample from the volumetric flask into a 100-ml. glass titration vessel. Add  $25.0 \pm 0.5$  ml. of methylene blue solution and  $10.0 \pm 0.5$  ml. of chloroform to the cylinder. (See NOTES.) Titrate with Solution 1 to the correct end point, rocking the cylinder carefully after each addition to avoid emulsions and maintaining temperature within prescribed limits of 70° to 90°F. by immersion in water if necessary. As the end point is approached, the rate of transfer of color increases and Solution 1 must be added dropwise with *vigorous* shaking after each addition. If the approximate titration is known, 80% of the required titrating solution should be added before shaking since this avoids emulsion trouble. Application of vacuum to the titration cylinder may help to break some emulsions.

After the first few additions, the blue color concentrates entirely in the chloroform layer, but as the titration proceeds, there is a slow transfer of the color to the water layer. The end point is reached when both layers have the same color intensity when observed in the viewing cabinet. The use of the viewing cabinet is necessary in both standardization and titration of samples. The end point is very sharp and 0.05 ml. will cause a distinct change in color distribution at (or near) the equivalence point. If the end point is overshot, a ml. or more of Solution 2 may be added and the sample again titrated with Solution 1.

The total volume of Solution 1 to be used in the calculation must be corrected by subtracting the equivalent volume of Solution 1 corresponding to the amount of Solution 2 used. The corrected volume of Solution 1 is *T*. (See NOTES.) The final end point should always be approached from the same direction.

Calculation.—

$$\text{Per cent Combined SO}_3 = \frac{T \times N \times 8.0}{\text{Wt. of sample in the aliquot}}$$

When a 5.0-g. sample is used and the normality of Solution 1 is 0.004:

$$\text{Per cent Combined SO}_3 = T \times 0.64.$$

where *T* = ml. Solution 1 corrected for any Solution 2 used.

*N* = Normality of Solution 1. (Should be calculated to at least 3 significant figs.)

$$\text{Per cent Active} = \text{per cent Combined SO}_3 \times \frac{\text{Mol. Wt. of Active}}{80}$$

NOTES.—The volumes of methylene blue solution and chloroform may be changed if found of advantage and if the same volumes are used in standardizing the reagents, Solutions 1 and 2.

The titration *T* should be as near 10 ml. as possible, preferably 8 to 12—never outside 5 to 15 ml.

## SOAPS HIGH IN COCONUT OIL

If desired, this method may be used for any soap. It is often called the "soda soap" method.

**Procedure.**—Proceed with the extraction as given above, except that the extracts are collected in a 250-ml. beaker or Soxhlet flask. Partially evaporate the ether to not less than 50 ml. on the edge of a steam bath and add 50 ml. of hot, neutral alcohol redistilled over caustic. Add several drops of phenolphthalein indicator and titrate with 1 *N* NaOH to exact neutrality. Evaporate on the steam bath to dryness, and while the soap is in the form of a thick paste, swirl the beaker on its side, thus distributing the soap in a thin layer along the sides and bottom of the beaker.

Dry to constant weight in an oven at  $105^{\circ} \pm 2^{\circ}\text{C}$ . After a preliminary drying at  $105^{\circ}\text{C}$ . for an hour, drying may be continued at  $150^{\circ}\text{C}$ . On removal from the oven, cool in a desiccator and weigh as soon as cool.

Correct for neutral salts in the caustic solution by determining the amount of salt per ml. by neutralizing 20 ml. of 1 *N* NaOH with 1 *N* HCl using phenolphthalein indicator and drying the residue to constant weight at  $105^{\circ}\text{C}$ . From the weight of the residue found, subtract the weight expected if the reagents had been 100% pure. The difference divided by 20 gives the correction per ml. for neutral salts. Subtract the product of the total fatty acid titration times the factor (0.022) plus correction for neutral salts from the weight of soda soap to obtain total fatty acids.

If the soap is a cold process soap containing superfat, i.e., unsaponified fat, and total fatty acids are required, it will be necessary to treat the sample after dissolving in water with 5 ml. (or more) of 50° Bé caustic potash solution. The solutions should be mixed thoroughly. With cover glass on the beaker, place over an opening in a steam bath, saponify for one hour with occasional stirring. Acidify with an excess of dilute  $\text{H}_2\text{SO}_4$  (1:4) and proceed as above.

If the real soap in a soap containing superfat is desired, it will be necessary to determine the superfat including free fatty acid and unsaponifiable matter and to correct the total fatty acid as determined without further saponification.

## UNSAPONIFIED AND UNSAPONIFIABLE MATTER

**Apparatus and Reagents.**—The extraction cylinder used is a 250-ml. glass-stoppered cylinder about 35 mm. in diameter and 300 mm. high. The solvent used is petroleum ether which should be of the pentane type, containing a minimum amount of iso-pentane, iso-hexane and hexane and conforms to AOCs Specification H2-41.

**Distillation Test.**<sup>4</sup>—Initial boiling point—not less than  $35^{\circ}\text{C}$ . nor over  $38^{\circ}\text{C}$ .

Dry flask end point—not less than  $52^{\circ}\text{C}$ . nor over  $60^{\circ}\text{C}$ .

At least 95%, distilling under  $54^{\circ}\text{C}$ .

Not over 60%, distilling under  $40^{\circ}\text{C}$ .

Specific gravity at  $15.5^{\circ}\text{C}$ .—0.630 to 0.660.

Color—water white. Doctor test—sweet.

Evaporation residue—not over 0.0011% by weight.

Copper strip corrosion test, ASTM—D130-56—Noncorrosive (p. 1999).

Unsaturated Compounds—trace only permitted.

<sup>4</sup> Distillation test to be made according to ASTM Method D216-32.

*Procedure*—Weigh a  $5 \pm 0.01$  g sample into a 250 ml beaker. Add 100 ml of 50% redistilled ethyl alcohol. Warm and stir to effect solution keeping the temperature under  $60^{\circ}\text{C}$ . Filter off any undissolved residue on a Gooch crucible with an asbestos or paper pad into an extraction cylinder. Wash 3 times with hot  $50^{\circ}\text{C}$  alcohol and then with 5 ml of hot 95% alcohol. Complete the washing with a small amount of petroleum ether.

Make the volume of solution in the cylinder up to the 160 ml mark with redistilled alcohol. Add 50 ml of petroleum ether. Stopper with a rubber stopper which has been soaked in petroleum ether overnight to remove soluble matter. Shake vigorously for one minute and allow to settle until both layers are clear. The volume of the upper layers should be about 40 ml. Draw off the petroleum ether layer as closely as possible by means of a slender glass siphon into a 500 ml pear shaped separatory funnel containing 25 ml of 10% alcohol containing a few drops of phenolphthalein. Take special care that none of the alcohol soap layer is drawn off. Repeat the extraction at least 6 times using 50 ml of petroleum ether each time. Draw all the extracts into the same separatory funnel. When extraction is completed stopper the separatory funnel and shake vigorously for 0.5 minute to wash the extract. Draw off the alcohol layer and swirl the funnel to collect any drops of the washing solution at the bottom. Continue washing with two 5 ml portions of 10% alcohol until the extract is free from alkali and soaps as shown by the absence of color in the alcohol layer. Transfer the washed extracts to a tared 150 ml Soxhlet flask and rinse the separatory funnel several times with petroleum ether. Evaporate the solvent in a gentle current of dry air on the steam bath. Dry in an oven at  $105^{\circ}\text{C}$  for 15 minutes. Cool and weigh. Dissolve the residue in 50 ml of warm ethyl alcohol neutralized to phenolphthalein with the same color as the original neutral alcohol with 0.04 N sodium hydroxide solution and calculate to oleic acid. Deduct this figure from the gross weight of the residue previously found. Any blank residue from the petroleum ether must also be deducted from the weight of the residue. Report results as Unsaponified and Unsaponifiable Matter.

### UNSAAPONIFIABLE MATTER

*Procedure*—Weigh  $5 \pm 0.01$  g of the sample into a 200 ml Erlenmeyer flask. Add 30 ml of redistilled 95% ethyl alcohol and add 5 ml of 50% aqueous KOH. Boil the mixture one hour under a reflux condenser. Transfer the solution to the extraction cylinder and wash the flask with 95% redistilled alcohol to the 40 ml mark. Complete the transfer first with warm and then cold water until the total volume is 80 ml. Then wash the flask with a small quantity of petroleum ether. Cool the cylinder and contents to room temperature. Add 50 ml of petroleum ether and proceed with the extraction as outlined under Unsaponified and Unsaponifiable Matter.

Weigh the residue and correct for fatty acids. Report the result as Unsaponifiable Matter. Deduct the unsaponifiable result from that of the unsaponified and unsaponifiable and report the difference as Unsaponified Matter.

For soaps containing lanolin many more extractions for Unsaponified and Unsaponifiable Matter will be required for complete removal. For any sample thorough and vigorous shaking is necessary in order to bring the two phases into the most intimate contact possible.

## FREE ALKALI OR FREE FATTY ACID

The methods outlined will not give absolutely accurate results for free alkali, but will give results sufficiently accurate for control or practical soap analyses. The accuracy is probably close to  $\pm 0.1\%$   $\text{Na}_2\text{O}$ .

*WHEN "BUILDERS" (OR FILLERS) ARE LOW IN AMOUNT  
AND ARE NOT DETERMINED*

*Procedure.*—Weigh a 20-g. sample ( $\pm 0.05$ ) rapidly and transfer to a 500-ml. Erlenmeyer flask containing 100 ml. of hot, neutral 95% alcohol. Cover the flask with a watch glass and dissolve the soap as rapidly as possible by heating on the steam bath. Add a few drops of phenolphthalein and titrate rapidly with 0.25 *N*  $\text{H}_2\text{SO}_4$  without filtering. Take the first end point, disregarding any subsequent return of color. Calculate to free  $\text{Na}_2\text{O}$  (or  $\text{NaOH}$ ) or  $\text{K}_2\text{O}$  (or  $\text{KOH}$ ) as the character of the soap indicates. If the alcoholic solution is acid to phenolphthalein, titrate with 0.1 *N*  $\text{NaOH}$  and calculate the percentage of free fatty acid as oleic acid, or lauric acid if coconut soap. Save the solution for determination of carbonates.

*WHEN "BUILDERS" ARE DETERMINED*

*Procedure.*—Weigh a  $10 \pm 0.02$ -g. sample and dissolve in 200 ml. of hot, neutral 95% alcohol. Filter through a 9-cm. filter paper into a 500-ml. Erlenmeyer flask and wash the residue three times with hot, neutral 95% alcohol. Protect from  $\text{CO}_2$  and other acid fumes during filtration. If the soap contains borax, or phosphates, it can be washed with alcohol indefinitely without removing the apparent alkalinity. Cover the flask with a watch glass and heat to incipient boiling. Titrate with 0.25 *N*  $\text{H}_2\text{SO}_4$  and report as free  $\text{Na}_2\text{O}$  (or  $\text{NaOH}$ ) or free  $\text{K}_2\text{O}$  (or  $\text{KOH}$ ) as the character of the soap indicates. If the alcohol is not pink, titrate with 0.1 *N*  $\text{NaOH}$  and report free fatty acid as oleic acid.

If potassium carbonate is present, the free  $\text{KOH}$  results will be high due to the solubility of  $\text{K}_2\text{CO}_3$  in the alcohol. For liquid soaps containing free  $\text{KOH}$  and  $\text{K}_2\text{CO}_3$  the following procedure has given satisfactory results: Weigh a 20-g. sample of the soap solution into a 500-ml. Erlenmeyer flask. Add 10 g. of neutral dry salt. Mix the salt with the soap thoroughly by shaking. Allow to stand 10 minutes covered by a watch glass. Add 20 ml. of hot, neutral 95% alcohol. Shake thoroughly and place on the steam bath for 10 to 15 minutes, shaking occasionally. Filter through a neutral filter paper moistened with neutral alcohol into another 500-ml. Erlenmeyer flask. Retain most of the insoluble in the flask, if possible. Wash with 25 ml. of hot alcohol, pouring around the top of the paper so as to wash the paper at the same time. Give the paper a slight additional wash with neutral alcohol after the first has drained through. Allow to drain. Titrate with 0.25 *N* or 0.5 *N* acid, and from this calculate free  $\text{K}_2\text{O}$ .

## TITER TEST

*Preparation of Total Fatty Matter (Fatty and Rosin Acids and Unsaponifiable Matter).*—Dissolve 200 g. of soap in 200 ml. of water in a 1-liter Erlenmeyer flask, add 20 ml. of 1:3 sulfuric acid and heat until the fatty matter collects in a clear layer.

The flask should be covered with a watch glass. Much time is saved by placing the sample in a 1-liter beaker and using a motor-driven stirrer to keep constant

agitation Siphon off the acid water layer and decant the fatty matter through a dry filter paper into tall form lipless 180 ml beaker If droplets of water can be seen refilter the fatty acids through a dry filter paper

**Procedure**—A standard titer thermometer (A O C S Specification H6-40) graduated at zero and in tenths degrees from 10° to 65°C is used or in 20 from -2°C to 66°C It should be certified by the United States Bureau of Standards or carefully standardized against a certified thermometer Special thermometers (graduated in tenths degree Centigrade) in 20°C ranges from 0°-80°C may be used

After the fatty acids are dry cool carefully by immersing in and out of water at about 17°C until a cloud begins to form stirring continuously with the thermometer (about 150 rpm) so that no crust forms on the sides or bottom of the beaker Care must be taken not to cool too rapidly or low results will be obtained Hold the beaker in the air and continue stirring more slowly (about 100 rpm) until the mercury remains stationary for 30 seconds or begins to rise within that time Wipe the outside of the beaker dry and carefully place the beaker and contents in a suitable container (air jacket) submerged in water or in ice salt water mixtures when necessary maintained at a temperature of 10°C below the titer For titers above 30°C the temperature should be 20°C Allow the thermometer to hang without any disturbance with the bulb in the center of the fatty acids and follow the thermometer readings Record the highest point to which the mercury rises as the titer of the fatty acids

When not enough soap or fatty matter is available the official method of the A O C S D-15-48 should be used This method which differs slightly in details and requires less fatty acids may also be used on the fatty acids obtained in the above procedure

### IODINE VALUE

The iodine value is determined on the fatty matter obtained in the above procedure for titer test by the Wijs method If rosin is present this method cannot be used<sup>5</sup>

**Reagents** Wijs Iodine Monochloride Solution See p 1439

Sodium Thiosulfate, Standard 0.1 N

Potassium Iodide Solution 5%

Chloroform U S P

Starch Indicator

**Procedure**—Weigh exactly a sample of such size that at least 100% to 150% of the amount of iodine absorbed remains in excess on a watch glass and transfer to a clean dry 500 ml glass stoppered bottle washing the watch glass thoroughly with 20-30 ml of chloroform Add 25 ml of iodine monochloride and at the same time prepare a blank with the same amount of chloroform and iodine monochloride Mix the contents gently and immediately put the bottles in a dark place at a temperature of 75°-90°F for exactly 30 minutes Add 20 ml of 5% potassium iodide to the sample and blank followed at once by 100 ml of water Titrate with 0.1 N sodium thiosulfate using starch solution as an indicator Do not add starch until the solution has a pale straw yellow color Toward the end of the reaction

<sup>5</sup> In case the iodine value must be obtained on samples containing rosin a 0.1 g sample is dissolved in 20 ml of glacial acetic acid and 20 ml chloroform in the glass stoppered bottle Immerse the bottle in water at a temperature of 21.5° - 22.5°C for 30 minutes Add the Wijs solution as above and maintain the temperature at 21.5° - 22.5°C for one hour Other operations are the same as above

stopper the bottle and shake violently. The number of cubic centimeters of standard thiosulfate solution used for the blank minus the amount used for the sample, gives the thiosulfate equivalent of the iodine absorbed by the amount of sample used in the determination. Calculate to per cent iodine absorbed. Mechanical agitation using a small variable-speed motor attached to a glass stirrer is an advantage. It is necessary to use a wide-mouth glass-stoppered bottle.

### SAPONIFICATION VALUE

*Procedure.*—Weigh exactly a 5-g. sample of the fatty matter obtained in the titer determination and wash into a 300-ml. Erlenmeyer flask with hot, neutral, redistilled 95% alcohol and add 50 ml. of an approximately 0.7 *N* alcoholic-potash solution. Prepare a blank in the same manner, omitting the sample. Insert a funnel in the neck of the flask and saponify for exactly one hour, swirling the contents occasionally. Cool quickly and titrate at once with 0.5 *N* hydrochloric acid, using phenolphthalein indicator. Calculate the milligrams of potassium hydroxide required to saponify one g. of fat by multiplying the difference between the blank and sample titrations by 5.61 and report as saponification value.

### FREE GLYCEROL

#### (Iodometric-Periodic Acid Method)

*Apparatus.* Buret.—50-ml., accurately calibrated.

Magnifier.—Meniscus, suitable to permit reading the buret to 0.01 ml.

Flask.—Volumetric, 1-liter glass-stoppered is preferred, but regular volumetric flasks and rubber stoppers may be used.

Pipets.—Volumetric, 10-ml., 25-ml., 50-ml., and 100-ml. The 25- and 50-ml. pipets must conform to Bureau of Standards tolerances and be accurately calibrated to deliver 25 and 50 ml., respectively.

Electric Stirrer.—Variable speed with glass stirrer.

*Reagents.* Periodic Acid ( $\text{H}_5\text{IO}_6$ ), Reagent Grade.—Manufactured by G. Fredrick Smith Chemical Company, Columbus, Ohio, or equivalent.

Soluble Starch.—Test for sensitivity: Place 2 ml. of starch indicator solution in 100 ml. of distilled water and add 0.05 ml. of 0.1 *N* iodine solution. The deep blue color produced must be discharged by 0.05 ml. of 0.1 *N* sodium thiosulfate.

Chloroform.—U.S.P. or reagent grade. Blank tests run on periodic acid with and without 50 ml. of chloroform must check within 0.5 ml. If they do not, get a new supply of chloroform.

Potassium Dichromate, A.C.S. Grade.—The potassium dichromate is finely ground and dried to constant weight at *ca* 110°C. before using. NOTE: A standard sample of potassium dichromate with a certificate of analysis may be obtained from the National Bureau of Standards, Washington, D. C. This sample is strongly recommended as the primary standard for this method. Treat as directed in the certificate of analysis accompanying the sample.

Periodic Acid Solution.—Dissolve 5.4 g. of periodic acid in 100 ml. of distilled water and then add 1,900 ml. of glacial acetic acid and mix thoroughly. Store the solution in a dark, glass-stoppered bottle or store in the dark in a clear, glass-stoppered bottle.

Sodium Thiosulfate Solution, 0.1 *N*.—Dissolve 24.8 g. of sodium thiosulfate in distilled water and dilute to 1 liter. Standardization: Pipet 25 ml. of the standard dichromate solution into a 400-ml. beaker. Add 5 ml. of hydrochloric acid, 10 ml.

of potassium iodide solution and rotate to mix. Allow to stand for 5 minutes and then add 100 ml of distilled water. Titrate with sodium thiosulfate solution stirring continuously until the yellow color has almost disappeared. Add 1 to 2 ml of starch indicator solution and continue titration adding the thiosulfate solution slowly until the blue color has just disappeared. The strength of the thiosulfate is expressed in terms of its normality

$$\text{Normality of Na}_2\text{S}_2\text{O}_3 \text{ solution} = \frac{2.5}{\text{Ml sodium thiosulfate solution required}}$$

**Potassium Iodide Solution**—Dissolve 150 g of potassium iodide in distilled water and dilute to 1 liter

**Starch Indicator Solution**—Make a homogeneous paste of 10 g of soluble starch in cold distilled water. Add to this 1 liter of boiling distilled water stir rapidly and cool. Salicylic acid (1.25 g per liter) may be added to preserve the indicator. If long storage is required the solution must be kept in a refrigerator at 4° to 10°C (40° to 50°F). Fresh indicator must be prepared when end point of the titration from blue to colorless fails to be sharp.

**Standard Potassium Dichromate Solution 0.1 N**—Dissolve 4.9035 g of finely ground and dried potassium dichromate in distilled water in a 1 liter volumetric flask and make up to volume at 25°C.

**Procedure**—Weigh approximately 10 g of sample to the nearest 0.01 g.

Add 91 ml of chloroform measured from a buret to within  $\pm 0.2$  ml to a 1 liter volumetric flask. Then add with a graduate 25 ml of glacial acetic acid.

Transfer the sample quantitatively to the volumetric flask and add approximately 500 ml of distilled water. Stopper and shake until sample is dissolved. If the soap does not react readily warm contents of the flask and shake. If warmed cool to room temperature before proceeding.

Add distilled water to mark stopper and mix thoroughly by inverting set aside until the aqueous and chloroform layers separate.

Pipet 50 ml of periodic acid reagent into a series of 400 ml beakers. Prepare two blanks by adding 100 ml of distilled water to each.

Pipet 100 ml of the aqueous solution into a 400 ml beaker containing 50 ml of periodic acid reagent. Shake gently to effect thorough mixing. Cover with a watch glass and allow to stand 30 minutes.

Add 20 ml of KI solution mix by gently shaking allow to stand at least 1 minute but never more than 5 minutes before titrating. Do not allow to stand in bright or direct sunlight.

Dilute to approximately 200 ml with distilled water and titrate with 0.1 N  $\text{Na}_2\text{S}_2\text{O}_3$  solution. Use the variable speed electric stirrer to keep the solution thoroughly mixed. Continue the titration to the disappearance of the brown iodine color. Add 2 ml of starch indicator solution and continue the titration to the disappearance of blue iodo starch color.

Read the buret to 0.01 ml.

The blanks are handled exactly like the sample.

If the titration of the sample is less than 0.8 of the titration of the blank repeat test using smaller portions (50, 25, 10, and 5 ml) until the titration of the sample is more than 0.8 of that of the blank. If 10 (or less) ml of sample solution is necessary to bring within limit required above repeat starting at the beginning with a smaller sample 2 g or less.

**Calculation.**—Report the free glycerol to the nearest 0.1%.

$$\text{Free glycerol, per cent} = \frac{(B - S) \times N \times 2.302}{W}$$

where  $B$  = titration of blank

$S$  = titration of sample

$N$  = normality of  $\text{Na}_2\text{S}_2\text{O}_3$  solution

$W$  = weight of sample represented by aliquot for procedure

$$W = \frac{\text{weight of sample} \times \text{ml. used in test}}{900}$$

**NOTES.**—Samples may be allowed to stand 1.5 hours at room temperature before titrating, but never longer. Do not allow to stand in bright or direct sunlight.

Cork stoppers must never be used where periodic acid can come in contact with them.

If soap contains more than 10% moisture, adjust the amount of chloroform added so that total volume of fatty acid and chloroform will equal 100 ml. = 1 ml.

If aqueous phase is alkaline due to large amounts of builder in the soap, add  $\text{H}_2\text{SO}_4$  sp. gr. 1.84 in 0.5-ml. increments until solution is definitely acid to litmus.

## TESTS FOR SYNTHETIC DETERGENTS

If preliminary tests have shown the presence of a synthetic detergent and the presence of soap as well, the soap can be determined in the alcohol-soluble material by extracting the fatty acids from an acidulated alcohol-water solution and weighing of the extracted fatty acids which must be corrected for any unsaponifiable material present. The synthetic detergent can be identified and determined in the alcohol-water heel from the extraction. The problem is simplified if soap is not present since the tests for synthetics can then be made directly on the alcohol-soluble portion of the sample.

Since organic builders will also be in the alcohol-soluble matter, it is important to determine if possible the nature of these builders by infrared examination before any attempt is made to further identify and assay the active ingredient. At this point qualitative tests for such elements as sulfur and nitrogen are in order. With these tests and the determination of the cationic  $\text{SO}_3$  by titration, a reasonable guess as to composition may be possible. Confirmation of these guesses can then be carried out. Two of the most common anionic detergents are the alkyl sulfates and the alkyl benzene sulfonates. These two materials will be used as examples in the following tests.

## UNSULFONATED OR UNSULFATED MATERIAL

The unsulfonated material from sodium alkyl benzene sulfonate will be alkyl benzene and the unsulfated from alkyl sulfate will be fatty alcohol. Both are low volatile materials and may be lost totally or in part during the alcohol separation, hence for an accurate determination the analysis should be carried out on the original sample, for a correction to the alcohol-soluble material, the analysis must be made on the alcohol-soluble portion itself.

**Reagents.** Alcohol, No. 30 or 3A denatured.

Potassium Hydroxide, 48 to 50 Bé.

Petroleum Ether, A.C.S. grade.

Sodium Dihydrogen Phosphate ( $\text{NaH}_2\text{PO}_4$ ), reagent grade.

**Apparatus.** Extraction Cylinder, 250 ml.



Separatory Funnel, 250 ml

Soxhlet Flask, 150 ml

**Procedure**—Weigh a suitable sized sample of the product. Dissolve in about 50 ml of hot alcohol transfer to a 250 ml extraction cylinder using sufficient alcohol to bring the volume to 80 ml. Add KOH sufficient to make *distinctly* alkaline. When the product is liquid or paste wash from the weighing dish with hot alcohol until the volume of alcohol equals 80 ml. Then continue washing with hot water. Add sufficient water to bring to 150 ml mark. Cool well below the boiling point of the solvent.

Extract with petroleum ether at least 5 times using 50 ml portions. Shake each extraction vigorously for 0.5 minute. Allow to settle well between extractions. Addition of a few grams of  $\text{NaH}_2\text{PO}_4$  crystals will eliminate emulsion troubles ( $\text{NaH}_2\text{PO}_4$  should not be used if any kind of soaps are present). Draw off the petroleum ether layers into a small separatory funnel. Add 30 ml distilled water and shake to mix the two layers. Draw off the water layer. Transfer the petroleum ether layer to a tared 150 ml Soxhlet. Evaporate in a gentle current of dry oil free air on top of the steam bath until no odor of petroleum ether remains. The Soxhlet must be removed at once as soon as petroleum ether has evaporated. A white mist in the neck of the Soxhlet is often noticeable when the solvent has evaporated. *Prolonged heating must be avoided* because the residue is readily volatilized. Cool in a desiccator and weigh.

**Calculations**—

$$\text{Per cent Unsulfonated or Unsulfated in sample} = \frac{\text{Wt of residue} \times 100}{\text{Wt of sample}}$$

When alcohol soluble is used

Per cent Unsulfonated or Unsulfated in alcohol soluble original sample basis

$$= \frac{\text{Wt of residue} \times \% \text{ alcohol soluble}}{\text{Wt of sample (or equiv wt of aliquot) alcohol soluble basis}}$$

### ESTER $\text{SO}_3$

The determination of Ester  $\text{SO}_3$  is dependent upon the hydrolysis of the sulfate ester and subsequent measurement of the  $\text{H}_2\text{SO}_4$  formed. If no interfering substances are present the  $\text{H}_2\text{SO}_4$  can be determined by titration. If however other hydrolyzable substances are present in the sample the  $\text{H}_2\text{SO}_4$  must be precipitated with  $\text{BaCl}_2$  after the removal of organic matter and weighed as  $\text{BaSO}_4$ . In general when  $\text{SO}_3$  is to be determined by titration the original sample should be used although the alcohol soluble portion of the sample may be used. When a gravimetric  $\text{SO}_3$  is necessary the determination must be run on the alcohol soluble portion.

**Reagents** Hydrochloric Acid, 0.1 N, accurately standardized

Sodium Hydroxide, 0.1 N, accurately standardized

Methyl Orange Indicator

Barium Chloride Solution 10% in distilled water

**Apparatus** Soxhlet Flasks 250 ml Pyrex

Condenser—Reflux condenser 12" water cooled

Burets—Regular equipment

**Ester  $\text{SO}_3$  by Titration Procedure.**—Weigh  $5.000 \pm 0.005$  g. of the sample into a 250-ml. or other suitable flask. For alcohol soluble, weigh  $1.000 \pm 0.001$  g. sample into a 250-ml. or other suitable flask. Dissolve in approximately 50 ml. of distilled water; add 2 to 3 drops of methyl orange indicator. Adjust carefully with  $N$  HCl (weaker solutions may be used) to the methyl orange end point. Then add 35 ml. of  $N$  HCl. Add several boiling pieces, attach a water cooled reflux condenser to the flask, and boil gently for at least 2 hours after foaming has ceased or become constant, and until the sample appears to be completely hydrolyzed. Samples that are known to hydrolyze readily may be hydrolyzed overnight by setting the flask covered with a watch glass on the steam bath. It is safest to then connect the flask to a reflux condenser and boil the contents of the flask, at least 0.5 hour. Cool and titrate with  $N$  NaOH to the methyl orange end point.

**Gravimetric  $\text{SO}_3$  Procedure.**—Weigh  $1.000 \pm 0.001$  g. of alcohol soluble or evaporate an equivalent aliquot of the filtrate from the alcohol-insoluble determination in a 250-ml. or other suitable flask. Add 50 to 100 ml. distilled water and 5 to 10 ml. concentrated HCl. Hydrolyze as for the titration procedure, above. Do not neutralize before hydrolysis. Wash the contents of the flask while still hot into a 250-ml. volumetric flask. Allow to cool to room temperature and dilute to the mark with distilled water. Mix thoroughly and allow to settle. (The fat layer should be above the volume mark on the flask.) Pour off or pipet off the fat layer and discard. The entire sample may be used by filtering off the fat and washing free of sulfates.

Pipet 100 ml. of the aqueous solution into a 400-ml. beaker and neutralize to methyl orange. Add 0.5 ml. of concentrated HCl and hot distilled water, if necessary, to bring the volume to 175 to 200 ml. Bring to boiling and while boiling, add 20 ml. of the barium chloride solution. Continue boiling gently for a few minutes. Then cover with a watch glass, place on the steam bath, and keep the beaker and contents at a temperature of  $70^\circ\text{C}$ . for 1 hour or until the precipitate settles well.

Decant the supernatant liquid through an ashless 9-cm. filter paper. Finally transfer the residue of barium sulfate in the beaker to the filter paper by means of a stream of hot water from a wash bottle and with aid of a policeman, if necessary. Wash the precipitate and paper thoroughly with hot water until the washings, when tested with  $\text{AgNO}_3$  solution, are shown to be free from chlorides.

Transfer the filter paper and precipitate to a tared porcelain crucible with the precipitate folded inside. Ignite, uncovered, at a low temperature in a muffle or over a Meker burner until the paper is consumed without inflaming. Burn off the carbon at as low a temperature as possible. After the carbon is burned, finally bring to a higher temperature (about  $900^\circ$  to  $1000^\circ\text{C}$ .) until completely ignited. If the muffle is used, the sample should be placed in a cold muffle and the temperature raised slowly or the paper burned off over a burner before placing the crucible in a hot muffle. If a burner is used, care must be taken to avoid loss due to drafts.

**Calculations. Ester  $\text{SO}_3$  by Titration.**—

When "as is" sample is used:

$$\text{Per cent } \text{SO}_3 = 8.0 \frac{(\text{Ml. } N \text{ NaOH} - \text{Ml. } N \text{ HCl})}{\text{Wt. of sample}}$$

2. When alcohol soluble is used: The ml. HCl are those used to hydrolyze the sample after neutralization to methyl orange. If other strengths than normal

solutions are used the necessary factors to cover must be used to convert the solutions used to normal basis For 1 g sample

Per cent Combined  $\text{SO}_3$  (Ester  $\text{SO}_3$ ) =  $8 \text{ (ml } \backslash \text{ NaOH - ml } \backslash \text{ HCl)}$

Gravimetric  $\text{SO}_3$  —

$$\text{Per cent } \text{SO}_3 = \frac{34.3 \times \text{weight of BaSO}_4}{\text{Wt of sample (or aliquot equivalent)}}$$

To convert these results to original sample basis multiply the percentages obtained by per cent Alcohol soluble/100

### COMBINED ALCOHOLS

**Reagents** Hydrochloric Acid, C.P Concentrated

Petroleum Ether

Alcoholic Potassium Hydroxide, Approximately 0.5 N

Hydrochloric Acid, 1.0 N

**Indicators** — Methyl orange and phenolphthalein

**Apparatus** Reflux Condenser — Allihn or Liebig type water cooled at least 12" long

Flask — 250 to 300 ml round bottom flask with a ground glass connection to fit the condenser is preferred A tight cork stopper may be used

**Miscellaneous** — 250 ml extraction cylinder separatory funnel Soxhlet flask siphon etc

**Procedure** — Weigh a sample chosen to yield from 1 to 3 g of alcohols into a 250 ml or other hydrolyzing flask Dissolve in 50 to 60 ml of distilled water Add 2 to 3 drops of methyl orange indicator and carefully neutralize with standard acid or alkali to the methyl orange end point (The titration may be used to calculate the alkalinity) Add 50 ml  $\backslash \text{ HCl}$  or more if necessary measuring the amount added accurately (The seat after hydrolysis may be used for Ester  $\text{SO}_3$ )

Connect the flask to a reflux condenser place on the steam bath overnight and then boil at least 0.5 hour or until the sample is completely hydrolyzed. The sample may be hydrolyzed directly by boiling although a preliminary heating on the steam bath will reduce foaming

When hydrolysis is complete cool the flask and contents to about 50 C drain the water from the condenser and wash down the condenser into the flask with a small amount of distilled water followed by a small amount of petroleum ether (Titration for ester  $\text{SO}_3$  may be made at this point) Transfer the contents of the hydrolyzing flask into the extraction cylinder and extract with several 40 to 50 ml portions of petroleum ether Collect the extracts in a separatory funnel In making the first extraction mix the solvent with the sample by gentle rocking without shaking to avoid forming an emulsion Later extracts may be shaken thoroughly Each extract should be shaken a minimum of 30 seconds A minimum of 5 extractions should be made

Wash the combined petroleum ether extract with 30 ml portions of water containing 10% ethyl alcohol by volume to remove any acid Care should be taken in water washing the extracts not to shake hard or a very troublesome emulsion will be formed A few crystals of salt will aid in breaking an emulsion Final wash should be neutral to methyl orange

If the ester  $\text{SO}_3$  is to be determined on this sample the water washings should be combined with the acid seat for ester  $\text{SO}_3$  by titration or for gravimetric  $\text{SO}_3$

Transfer the washed extract to a tared Soxhlet. Evaporate off most of the solvent carefully, avoiding the use of much air. Continue to dry on top of the steam bath, without exposure to direct steam, until all solvent is off. Run an evaporation blank using a known weight of fatty alcohol and 200 ml. of petroleum ether at least weekly to insure that the technique used by the analyst will neither lose fatty alcohol nor leave petroleum ether in the total fat weighed.

**Calculations.—**

$$\text{Per cent Total fatty alcohols} = \frac{\text{Wt. of residue} \times 100}{\text{Wt. of sample}}$$

Per cent Combined fatty alcohols =

per cent Total alcohols — per cent Unsulfated or free alcohols

### TOTAL COMBINED $\text{SO}_3$ <sup>a</sup>

This determination is run on the alcohol-soluble material when it is desired to determine organically combined  $\text{SO}_3$ . The original sample should be used when total  $\text{SO}_3$  is desired.

The materials used in this analysis require caution in handling so that it is necessary for an analyst to become familiar with all details of procedure and the precautions before starting an analysis.

It is very important that the sample be dry. The alcohol soluble is dry and should need no further drying. Samples of other material which are not dry should be weighed into the fusion cup in sufficient size to give the equivalent of, but not over, 0.3 g. of organic matter after drying. Care must be taken in drying to avoid loss of volatile sulfur-containing material. The sample in the cup is then dried in an oven and cooled to room temperature before adding the reagents.

**Reagents.** Sodium Peroxide.—Parr calorific grade, finely powdered. Parr Instrument Company, Moline, Illinois.

**Benzoic Acid.**

**Potassium Perchlorate.**—Parr calorific grade, powdered. Parr Instrument Company, Moline, Illinois.

**Barium Chloride Solution.**—10%  $\text{BaCl}_2$  solution.

**Apparatus.** Instruction Manual.—Parr Instrument Co., Moline, Illinois, Manual No. 121.

**Flame Ignition Method.** *Bomb Apparatus.*—Parr Instrument Company, Catalog No. 2101, but without ignition housing. Includes AC3E bomb with 2ACN, 94% Ni fusion cup and A7AC5 Ni plated brass cover, wrench, bench socket, peroxide dipper, mixing rod, one dozen extra gaskets (specify lead gaskets) and Manual 121.

**Guard.**—The guard is made from a piece of 4" pipe, 6" long, mounted on 3 legs 10" long. The bomb is carried in a ring of a diameter to allow the fusion cup to fit into it. The ring is supported by rods fastened to the walls of the guard. A  $\frac{3}{8}$ " steel rod extending through the walls of the guard so as to just pass over the top of the bomb prevents the bomb falling out during ignition.

**Mirror.**—A mirror, metallic preferred, should be placed on the table below the guard and burner to enable the operator to observe the bomb during and after firing with a flame.

**Burner.**—A blast lamp or burner which can be adjusted to give a small pointed flame.

<sup>a</sup> Reproduced with permission from the Parr Manual 121, Parr Instrument Co., Moline, Illinois.

**Electric Ignition Method Bomb Apparatus**—Parr Instrument Company, Catalog No 2001 Includes AC2E bomb with 2ACN, 94% Ni cup and A7AC5 Ni plated brass cover, wrench, bench socket peroxide dipper, fuse wire, mixing rod, water bath, one dozen extra gaskets (specify lead gaskets), ignition unit and Manual 121

**Spatulas**—A small thin spatula is convenient for stirring the bomb charge. A second one is necessary to scrape off the spatula after use.

**Goggles**—Safety goggles Chipper's model dust proof should be used when handling the materials into the bomb to protect the eyes from premature explosion. Sodium peroxide thrown into the eyes might cause blindness.

**Procedure Flame Ignition**—Weigh  $1.0000 \pm 0.0001$  g of the original sample or  $0.3000 \pm 0.0001$  g of the dry alcohol soluble material into the dry fusion cup on an analytical balance. *If the sample contains water, dry in an oven before continuing.* It is extremely important that a sample containing no more than 0.30 g of organic material be used.

**Caution**—Before continuing be sure that the precautions below are noted.

Weigh  $0.30 \pm 0.01$  g benzoic acid powder on a torsion balance. Transfer to the fusion cup. Weigh  $1.00 \pm 0.01$  g powdered potassium perchlorate on the torsion balance. Transfer to the fusion cup.

Put on goggles and/or use safety shield. Use a spatula, platinum wire, or stirring rod. Carefully mix the contents of the fusion cup to obtain a homogeneous mixture. Fill one measure, approximately 15 g, of sodium peroxide. Then add the peroxide on top of the contents of the fusion cup without mixing. Brush any particles of peroxide off of the top rim of the cup. Place the cover on at once using a lead or asbestos gasket. Close the cup by pulling the fittings tightly into place. Shake the bomb to thoroughly mix the constituents. *The bomb should not be held in the bare hands and should preferably be shaken behind a metal shield.*

Place the bomb into the ring in the guard. Place the rod in position over the top of the bomb. Ignite contents of the bomb by applying small sharply pointed flame of the blast lamp to the bottom. Evidence of reaction and complete fusion is indicated by a slight noise and/or a dull redness at the point of fusion. As soon as this is noted, remove the flame.

Allow the bomb to stand about one minute to complete reaction. Remove from the guard and cool under the tap or by standing. When cool, remove cover and place the bomb on its side in a 400 ml beaker. Wash off the cover into the beaker with a watch glass, and cautiously add 100 to 150 ml hot water. Allow the fusion to dissolve completely.

Carefully remove the fusion cup, wash with hot distilled water, collecting the washings into the beaker. Neutralize the solution by slowly adding about 30 ml of HCl (concentrated CP). The neutral point can generally be recognized when the solution changes from a turbid dark color to a clear lighter color. Sufficient acid should be present to give about 0.5 ml excess per 200 ml of volume. *Excess acid must be avoided.*

**Electric Ignition**—Prepare charge in bomb exactly as described in the flame ignition procedure, above except insert a 7 cm length of fuse wire attached to electrodes as described in Parr Manual 121, Section C. A lead gasket must be used. Follow these instructions carefully observing all precautions. These are included for the protection of the analyst. Dissolve and neutralize the ignited contents of the bomb as described in the last paragraph under the flame ignition procedure.

Filter the solution into a 400 ml beaker and wash the filter until free from chlorides. The volume of the solution should be about 250 to 300 ml. Heat to boiling. While boiling, add all at once 15 to 20 ml of 10%  $\text{BaCl}_2$  solution. Con

tinue boiling for a few minutes; cover with a watch glass. Place on the steam bath and keep contents of beaker hot, approximately 70° to 80°C., for one hour, or until the precipitate has settled well. Often overnight is an advantage.

Test the clear upper layer with a few drops of  $\text{BaCl}_2$  solution to insure precipitation is complete. If so, decant the clear layer through a 9-cm. ashless filter paper. Then transfer the  $\text{BaSO}_4$  from the beaker to the paper by means of a stream of hot, distilled water from a wash bottle and with the aid of a policeman. Wash thoroughly with hot water until the washings show no chlorides when tested with  $\text{AgNO}_3$ .

Transfer the chloride-free residue and filter paper to a weighed porcelain crucible. Ignite the paper at a low temperature so that the paper shall char without flaming. The carbon should be burned off at as low a temperature as possible with the crucible uncovered. After the carbon is burned, the temperature should be raised to about 800°C. If the muffle is used, the sample should be placed in a cold muffle and the temperature raised slowly, or the paper burned off over a burner before placing the crucible in a hot muffle. If a burner is used, care must be taken to avoid loss due to drafts. Moisten the precipitate with 2 drops of concentrated  $\text{H}_2\text{SO}_4$  and reheat to remove the excess acid. Cool and weigh.

**Optional Procedure.**—When vacuum filtering is used, follow the procedure through "Test the clear upper layer with a few drops of  $\text{BaCl}_2$  solution to insure precipitation is complete." If so, decant the clear layer through a tared medium porosity (No. 4010) Selas filtering crucible into a liter Pyrex vacuum flask. Transfer the  $\text{BaSO}_4$  precipitate from the beaker to the crucible with a stream from wash bottle against sides of crucible so as not to lose precipitate by splashing.

When precipitate is free of chlorides by test of filtrate with silver nitrate, transfer crucible with precipitate to 105°C. oven to drive off water (approximately 0.5 hour) or heat gently to avoid spattering.

To make test for chlorides on filtrate cut vacuum to desired flask, remove crucible adapter and suspend a 25-ml. test tube by a fine string into the flask. Replace crucible adapter, apply vacuum and catch a few ml. of wash solution. Remove test tube and add a few drops of 0.1  $N$   $\text{AgNO}_3$ .

Transfer to muffle for ignition at 600° to 650°C. for 30 minutes. Cool in a desiccator and weigh rapidly.

Calculation.—

$$\text{Per cent SO}_3 \text{ (Parr bomb)} = \frac{\text{Wt. of ignited residue (BaSO}_4) \times 34.3}{\text{Wt. of sample (or sample equivalent of aliquot)}}$$

For 0.300-gram sample:

Per cent  $\text{SO}_3$  in alcohol soluble (Parr bomb), original sample basis

$$= \text{Weight of ignited residue} \times 1.143 \times \% \text{ alcohol soluble.}$$

**NOTES AND PRECAUTIONS.**—Thousands of determinations have been made with Parr sulfur bombs in many different laboratories. Where directions are closely followed and proper care is taken, these determinations have invariably been successful. However, you are dealing with materials which have explosive properties, if wrongly handled. In all determinations the following precautions *must* be taken: The full 15 grams of sodium peroxide must be used.

All lumps in the peroxide, perchlorate, and benzoic acid must be removed or crushed before weighing.

Best results are obtained when the sample is finely divided and, if possible, powdered. The charge must be thoroughly and completely mixed.

The gasket must be in good condition. Lead gaskets are supplied with all peroxide bombs and have been found satisfactory in almost all instances as their use eliminates all danger of a reaction between them and the fusion. Use only 1 gasket.

The cap or cover of the bomb must be properly seated on the gasket.

The screw cap must be screwed down tight.

Do not allow sodium peroxide or potassium perchlorate to come into contact with paper or other organic matter in waste cans or on the floor.

Discard the fusion cup if the sides or bottom have become visibly swollen or if the interior surfaces become worn or corroded to an inside diameter of 1.08 or more at any point or if the bottom shows appreciable etching or cracking. An inside diameter of 1.08 inches or more indicates the wall thickness has diminished to  $\frac{1}{64}$  inch or less. Wear can be followed by weighing the bomb after each use. Since the loss of weight is all from the lower  $\frac{1}{2}$  and the bottom, a safe loss limit can be established.

Directions for the Parr Sulfur Bomb. The Parr Instrument Co., Moline, Ill., should be available and read by the operator before starting the use of these bombs.

## ORGANIC BUILDERS

Organic builders will normally be found in the alcohol soluble material. Carboxy methyl cellulose is an exception since it is alcohol insoluble. However sodium glycolate which is frequently found in commercial carboxy methyl cellulose is alcohol soluble and should be suspected if carboxy methyl cellulose is a builder. Amides are frequently used as builders. They may be analyzed by a direct nitrogen determination or by hydrolysis and measurement of the fatty acids formed. Although many organic builders have been used in detergent products, space does not permit us here to attempt a systematic builder procedure. Suffice it to say that if a builder is suspected or known to be present, tests for assay must be devised depending upon other materials present.

## INORGANIC BUILDERS IN THE ALCOHOL INSOLUBLE

The alcohol insoluble material will contain most of the inorganic builders used in detergents plus carboxy methyl cellulose and some other infrequently used material such as starch and proteins. The tests usually carried out on the alcohol insoluble material include tests for alkalinity, phosphates, sulfates, carbonates, silicates, borates and water insoluble material. Tests for these materials follow. While chlorides may occur in either the alcohol soluble or insoluble portions of the sample or in both, their determination is shown in this section.

### ALKALINITY

( $\text{NaOH}$ ,  $\text{Na}_2\text{CO}_3$  or  $\text{NaHCO}_3$ )

**Procedure**—Weigh  $5.000 \pm 0.001$  g. of the sample into a 400 ml beaker. Dissolve in 100 to 150 ml warm water (about  $35^\circ\text{C}$ ). Add 2 drops of methyl orange and 2 drops of phenolphthalein.

If acid to methyl orange. Titrate with  $N$   $\text{NaOH}$  carefully to the methyl orange end point. Note reading which will be calculated to %  $\text{NaHSO}_4$ .

If alkaline to methyl orange and acid to phenolphthalein. Titrate with  $N$  acid to the methyl orange end point.

If alkaline to phenolphthalein. Titrate with normal acid to first the phenolphthalein and then the methyl orange end points.

If  $(2P - MO) > 0$

$$\text{Per cent NaOH} = (2P - MO) \times 0.80$$

$$\text{Per cent Na}_2\text{CO}_3 = 2(MO - P) \times 1.06$$

If  $(2P - MO) = 0$ , or  $<0$ :

$$\text{Per cent Na}_2\text{CO}_3 = 2P \times 1.06$$

$$\text{Per cent NaHCO}_3 = (MO - 2P) \times 1.68$$

COMMENTS.—When it is desirable to do so,  $\text{CO}_2$  can be determined by evolution and absorption in a weighed ascarite tube.

### CHLORIDES

Chlorides may be determined on the original sample, the alcohol-insoluble portion or on the alcohol-soluble matter, and should be reported on these bases, the total chlorides as  $\text{NaCl}$  being reported for the analysis of the original sample.

*Apparatus.* pH Meter, with silver and calomel electrodes.

*Reagents.* Silver Nitrate, 0.1 *N*, accurately standardized.

*Procedure.*—Weigh to  $\pm 0.001$  g. a sample approximately equal in grams to the per cent  $\text{NaCl}$  expected, but the sample should not exceed 10 g.

Dissolve in 250 ml. of hot distilled water, add 2 drops of methyl orange indicator and acidify to the acid color by adding  $\text{HNO}_3$  (1:4). Warm slightly and stir to effect maximum solution. Add 50 ml. of acetone.

Clean the silver electrode in the  $\text{HNO}_3$  (1:1) containing  $\text{NaNO}_2$ . Set up the titration cell with the silver electrode connected to the top terminal, the saturated calomel cell connected to the bottom terminal. Set the pH meter on + mv. Start the stirring and titrate the solution potentiometrically as follows: Add 0.5 ml. of  $\text{AgNO}_3$  solution and measure emf. If appreciable chloride is present, the emf should be in the range of 100 mv.

Add  $\text{AgNO}_3$  solution slowly in 2- to 3-ml. portions until the emf reaches 200 mv. Stir well.

Add  $\text{AgNO}_3$  solution in 0.1-ml. portions, allowing sufficient time after each addition for the solution to reach equilibrium (60 to 80 sec.). Measure the emf (stirrer off) at each 0.1-ml. point.

Calculate the end point by the rate of change method. The end point is usually in the range of 260 to 270 mv.

Example.—The method for determining the maximum rate of change is as follows:

<i>ml.</i>	<i>EMF</i>	$\Delta E$	$\Delta E'$
21.2	210	10	10
21.3	220		
		20	17 <sup>a</sup>
21.4	240	37	
		12	
21.5	277		25
21.6	302		

<sup>a</sup> Maximum rate of change.

$$\begin{aligned} \text{End point} &= 21.4 + \left( \frac{17}{17 + 12} \times 0.1 \right) \\ &= 21.46 \text{ ml.} \end{aligned}$$



Run a blank and subtract the value obtained from the value calculated above  
**Calculation** —

$$\text{Chlorides as NaCl per cent} = \frac{(S - B) \times N \times 5.85}{\text{Weight of Sample}}$$

where  $S$  = titration of sample

$B$  = titration of blank and

$N$  = normality of  $\text{AgNO}_3$

## SILICATES

**Apparatus** Evaporating Dish—Platinum or porcelain capacity ca 100 ml

Crucible—Platinum capacity 30 ml

**Procedure**—Weigh a portion of the alcohol insoluble material sufficient to contain approximately 0.2 g  $\text{SiO}_2$  into an evaporating dish. Add 50 ml of distilled water neutralize carefully with  $\text{HCl}$  and then add from 5 to 10 ml of  $\text{HCl}$  in excess. Keep the dish covered with a watch glass during this addition to prevent loss from spattering.

Evaporate to dryness on a steam or water bath or on a hot plate at a temperature not exceeding 120°C. Cool the residue and moisten with  $\text{HCl}$  let stand 5 to 10 minutes and then break up all lumps with a stirring rod.

Add ca 25 ml of hot distilled water to the residue heat for a few minutes and filter through a small ashless filter paper. Wash the paper and contents thoroughly with hot water. Repeat the above treatment beginning with. Evaporate to dryness. Filter through a second filter paper.

Place the 2 filter papers in a tared platinum crucible and ignite carefully first at a low temperature until the paper is consumed and then over a burner or in a muffle at a bright red heat (850 to 950°C). Cool to room temperature in a desiccator and weigh. Repeat until constant weight is obtained.

For the most accurate results moisten the weighed contents of the crucible with water add 10 ml of  $\text{HF}$  4 drops of  $\text{H}_2\text{SO}_4$  and evaporate to dryness over a low flame. Ignite as directed above cool to room temperature in a desiccator and weigh.

**Calculation**—When  $\text{SiO}_2$  is weighed

$$\text{Sodium silicate (1 Na}_2\text{O } 3.25 \text{ SiO}_2) \text{ per cent} = \frac{\text{Weight of SiO}_2 \times 131.8}{\text{Weight of Sample}}$$

When  $\text{SiO}_2$  is volatilized with  $\text{HF}$

$$\text{Sodium silicate (1 Na}_2\text{O } 3.25 \text{ SiO}_2) \text{ per cent} = \frac{(A - B) \times 131.8}{\text{Weight of Sample}}$$

where  $A$  = weight of crucible and contents before volatilization with  $\text{HF}$

$B$  = weight of crucible and contents after volatilization with  $\text{HF}$

## PHOSPHATES

This method determines all the phosphates as phosphorus pentoxide by conversion to the ortho form by acid hydrolysis and titration between pH 4.3 and pH 8.8 ( $\text{NaOH} - \text{P}_2\text{O}_5/2$ )

Applicable to any species of alkali metal phosphates free from interfering ions  
**Apparatus** Electrometric Titration Apparatus—Equipped with glass and calomel electrodes. Any standard pH meter capable of performing titrations accurate to  $\pm 0.1$  pH is suitable. Accurately standardized at pH 4.0 and 8.0

**Gas Burners.**—Preferably of the chimney or Argand type.

**Muffle Furnace.**—With suitable pyrometer and controls for maintaining temperatures up to 550°C.

**Evaporating Dish or Large Crucible,** porcelain or silica.

**Motor Stirrer,** air or electric.

**Reagents.** Standard Sodium Hydroxide, 0.5 or 1.0 *N*, carbonate free.

**Sodium Hydroxide Solution.**—Concentrated, approximately 50% by weight, carbonate free. A more dilute solution may be used. NaOH solutions must be protected from carbon dioxide contamination.

**Hydrochloric Acid,** concentrated, sp. gr. 1.19, reagent grade.

**Mixed Indicator (Optional).**—32 ml. methyl orange—0.05% in water.

32 ml. phenolphthalein—0.50% in 50% alcohol.

8 ml. thymol blue—0.04% in water.

4 ml. methylene blue—0.10% in water.

24 ml. alcohol, 95%, U.S.S.D. Formula 30 or 3A.

The individual components are stable indefinitely. The mixed indicator should be prepared at least weekly.

In practice 3 ml. of this mixed indicator are used in a final volume of approximately 250 ml. of solution to be titrated. The lower end point is taken as the first change from gray to a definite green; the upper end point is the change from pink to a bright purple.

**Procedure.**—The optimum size of sample is given by the formula:

$$\text{Sample, g.} = \frac{280 \times N}{\text{Per cent P}_2\text{O}_5 \text{ expected}}$$

where *N* = normality of NaOH to be used in titration

Soap products may be analyzed by using the filtrate from the SiO<sub>2</sub> determination. Use care not to exceed the sample weight prescribed above. Alternatively the sample may be prepared as described in the paragraph to follow.

Built synthetic products may be analyzed by using the alcohol-insoluble portion, but the following procedure is more rapid and quite as accurate. Weigh a sample, of size chosen by the formula above (but do not exceed 10 g.) to the nearest 0.001 g. Place sample in a porcelain or silica evaporating dish, or large crucible, and ignite gently over a low gas burner until most of the volatile combustible matter is burned off. Transfer to a muffle, operated at not over 550°C., for 10 to 15 minutes. The ignited residue need not be free from carbon and usually is of a grayish color. Cool and add cautiously 10 ml. concentrated HCl. Evaporate to dryness, take up with 50 ml. distilled water, 10 ml. concentrated HCl, and transfer to a 400-ml. beaker.

Each solution in a 400-ml. beaker, prepared as described above, should have a volume of about 100 ml. and contain an excess of at least 10 ml. concentrated HCl. Cover with a watch glass and boil for a minimum of 30 minutes, and up to 60 minutes in the presence of phosphates of the glassy type. Cool to room temperature (20°–30°C.).

Dilute to 200-ml. volume, place on electrometric titration stand and neutralize to 4.3 pH. Most of the neutralization may be made with 50% NaOH solution, but final adjustment should be made with the standard NaOH to be used in titration (0.5 or 1.0 *N*). Cool again, if necessary, to maintain temperature below 30°C.

Now titrate carefully to the 8.8 pH upper end point recording the titration between end points as  $T$

Calculations —

$$\text{Per cent Total } P_2O_5 = \frac{T \times N \times 7.098}{\text{Weight of Sample}}$$

where  $N$  = normality of NaOH

$T$  — titration between pH 4.3 and pH 8.8 end points

**NOTES**—The mixed indicator may be used for this titration but with some small sacrifice of accuracy. If the samples have been prepared by the ignition method they must be filtered and the paper washed thoroughly after the acid hydrolysis as particles of carbon obscure the visual end point. The color changes can be checked by comparison with pH meter readings to acquire familiarity with the exact shade required. For greatest accuracy titration with a pH meter is recommended.

**Interferences** Heavy metals such as Fe, Al, Ca, Mg, etc. which will precipitate either as insoluble phosphates or hydroxides before the upper end point is reached of course will interfere. Interference also occurs if borates, sulfites, carbonates or other buffering materials are present. The last two and much of the borate will be expelled during the acid hydrolysis boil.  $NH_4OH$  or other weak bases also will interfere. The most common interference is from silicic acid. Experiment and experience in analysis of sprayed and synthetics have shown that unless the ratio of %  $SiO_2$ /%  $P_2O_5$  approaches or exceeds 0.2 the interference by silicates will be so slight that it may be neglected. Larger amounts must be dehydrated and removed by filtration during the preparation of the sample.

## SULFATES

The percentage of sodium sulfate is determined in the alcohol insoluble portion of the sample by precipitation of the sulfate with  $BaCl_2$ .

**Reagents** Barium Chloride Solution 10% in distilled water

Bromine Water saturated solution

**Procedure**—Use the entire alcohol insoluble portion of the sample or weigh a suitable size portion thereof into a 600 ml beaker.

Add 200 ml of distilled water to the beaker and neutralize with concentrated HCl adding sufficient acid to give about 0.5 ml in excess.

If the solution is not clear it should be filtered and the paper washed until free from chlorides. The volume of solution from this point should be about 250 to 300 ml.

Heat to boiling. While boiling add all at once 15 to 20 ml of 10%  $BaCl_2$  solution. Continue boiling for a few minutes cover with a watch glass. Place on the steam bath and keep contents of beaker hot approximately 70° to 80° C for one hour or until the precipitate has settled well. Often overnight is an advantage.

Test the clear upper layer with a few drops of  $BaCl_2$  solution to insure precipitation is complete. If so decant the clear layer through a 9 cm ashless filter paper. Then transfer the  $BaSO_4$  from the beaker to the paper by means of a stream of hot distilled water from a wash bottle and with the aid of a policeman. Wash thoroughly with hot water until the washings when tested with  $AgNO_3$  show no chlorides.

Transfer the chloride free residue and filter paper to a weighed porcelain crucible. Ignite the paper at a low temperature so that the paper shall char without inflaming. The carbon should be burned off at as low a temperature as possible with the crucible uncovered. After the carbon is burned the temperature should be raised to about 800°C. If the muffle is used the sample should be placed in a cold muffle and the temperature raised slowly or the paper burned off over a

burner before placing the crucible in a hot muffle. If a burner is used, care must be taken to avoid loss due to drafts. Moisten the precipitate with 2 drops of concentrated  $\text{H}_2\text{SO}_4$  and reheat to remove the excess acid. Cool and weigh.

Calculations.—

$$\text{Per cent Na}_2\text{SO}_4 = \frac{\text{Wt. of barium sulfate} \times 60.86}{\text{Wt. of sample}}$$

### BORATES <sup>†</sup>

(In the Absence of Phosphates)

Apparatus.—pH Meter.

*Reagents.* Hydrochloric Acid.—(1:1), dilute 1 volume of hydrochloric acid (sp. gr. 1.19) with 1 volume of distilled water.

Mannitol, C.P.

Methyl Red Indicator Solution, prepared by dissolving 0.10 g. of methyl red in 100 ml. of a 50/50 mixture of ethyl alcohol and water.

$\alpha$ -Naphtholphthalein Indicator Solution.—Prepared by dissolving 0.10 g. of  $\alpha$ -naphtholphthalein in 100 ml. of a 50/50 mixture of ethyl alcohol and water.

Sodium Hydroxide Solution, 25% by weight, carbonate free.

Sodium Hydroxide Solution, 0.05 *N* or 0.1 *N* accurately standardized and carbonate free.

*Procedure.*—Accurately weigh a sample of the alcohol insoluble conforming to the following table, into a 250-ml. beaker:

<i>Estimated borate, %</i>	<i>Sample weight, g.</i>
0-10	2.0
10-25	1.0
25-50	0.75
50-90	0.50
90-100	0.40

Add 100 ml. of distilled water and warm on the steam bath until the sample has dissolved.

Make just acid to methyl red indicator with 1:1 hydrochloric acid and add 0.5 ml. of acid in excess. Cover the beaker with a watch glass and heat to simmering temperature for 10 minutes.

Cool the solution in a cold water bath to room temperature. Rinse the watch glass with water and add the washings to the solution. Insert the electrodes of a pH meter and bring the solution to a pH of approximately 6.3 by the dropwise addition of 25% sodium hydroxide solution. Titrate to exactly pH 6.3 with 0.05 *N* sodium hydroxide solution.

Add 5 g. of mannitol, stir until dissolved, and titrate to a pH of 8.0 with 0.05 or 0.1 *N* sodium hydroxide depending on the amount of borax present. The titration should be carried out in cold solution (room temperature or less). Record the buret reading.

Conduct a blank as follows: Take a volume of boiled distilled water corresponding to the volume of solution at the end of the titration. Add 0.5 ml. of 1:1 hydrochloric acid. Insert the electrodes by a pH meter and bring the solution to

<sup>†</sup> Bernstein and Haftel, The Determination of Borax in Soap, J. Am. Oil Chemists' Soc., 27, 45, 1950.

a pH of approximately 6.3 by the dropwise addition of 25% sodium hydroxide solution. Titrate to exactly pH 6.3 with 0.05 N sodium hydroxide solution. The volume of 0.05 N sodium hydroxide required is not recorded.

Add 5 g of mannitol and stir until dissolved. Titrate to a pH of 8.0 with the same strength sodium hydroxide as employed above. Record the buret reading. The blank should not exceed 0.1 ml and is usually less. (See NOTES)

Calculations —

$$\text{Borates as Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O, per cent} = \frac{(A - B) \times N \times 9.536}{\text{Weight of sample}}$$

where  $A$  = ml NaOH to titrate sample

$B$  = ml NaOH to titrate blank

$N$  = normality of NaOH solution

NOTES—Distilled carbon dioxide free water should be employed throughout this procedure.

An indicator end point may be employed when a pH meter is not available. In the latter event proceed as follows. Starting with the acidulated solution, cool in a cold water bath to room temperature. Rinse the watch glass with water and add the washings to the solution. Add several drops of methyl red indicator solution and 1 l hydrochloric acid dropwise until the solution is distinctly acid to the indicator. Titrate with 0.05 N sodium hydroxide to the methyl red end point (pure yellow). Record the buret reading. Add 5 g of mannitol and stir until dissolved. Add 3 ml of  $\alpha$ -naphtholphthalein indicator solution and titrate the boric acid complex with 0.05 or 0.1 N sodium hydroxide to a green yellow end point. The titration should be carried out in cold solution (room temperature or less). A blank should be run on the amount of mannitol used in the titration. The blank should not exceed 0.1 ml and is usually less.

Methyl purple (available from laboratory supply companies) can be used to advantage in place of methyl red if so desired.

## MISCELLANEOUS TESTS

### DETERMINATION OF pH

**Reagents** Distilled Water—Freshly boiled cooled distilled water adjusted by the laboratory to a pH of 6.0 to 7.0. Store in Pyrex glass stoppered by rubber or glass stoppers, not corks.

**Buffers**—In the ranges needed.

**Apparatus** pH Setup—The Leeds and Northrup Portable Universal pH Indicator Unit, the Beckman Laboratory Model assembly or equivalent.

**Electrodes**—Glass Beckman 1190 or equivalent for L & N models 5" long with 30" lead wire. Calomel Beckman 1170 or equivalent for L & N models 5" long with 30" lead wire.

**Procedure**—Follow the manufacturer's instructions for standardization and operation of the pH Meter. Buffer the instrument in the range needed for the sample.

Dissolve 0.5 grams of sample in 100 ml distilled water and read the pH at 25° to 30°C.

### WATER INSOLUBLE

Proceed as in the determination of alcohol insoluble material. After filtering and thoroughly washing the residue, extract it with water at 60°C and wash the filter thoroughly. (When the matter insoluble in water is all inorganic boiling water may be used for the extraction and washing.) Dry the filter and residue.

at 100° to 105°C. for 3 hours, cool, and weigh matter insoluble in water. The nature of this matter may be determined by further examination.

### COMMENT

When more detailed information is needed and when additional tests are required, reference should be made to the Official and Tentative Methods of the American Oil Chemists' Society or to the ASTM Standards of the American Society for Testing and Materials.

samples from each of these subdivisions if the area is of great extent, or if it is not uniform with respect to soil properties, plant growth, or land management and use. The number of sampling units taken to make up the sample should be governed by the variability of the characteristic under test and the degree of accuracy of the estimate desired. Twenty or 30 sampling units for surface horizons and 10 sampling units for lower horizons have been suggested as minimum values for some purposes. It should be stressed that these minima are arbitrary and, in many cases, a considerably greater number of sampling units may be advisable. The sampling units should be taken from sites chosen at random within the sampling area.

*Sampling Tools.*<sup>4</sup>—The ideal sampling tool is one that gives an uncontaminated, reproducible sampling unit of approximately uniform cross-section to the desired depth. Augers of the wood-bit or post-hole type are often used but are not very satisfactory from the standpoint of the above criteria. Sampling tubes are quite satisfactory, particularly for sampling surface horizons, but they cannot be used on stony or dry, sandy soils. Subsurface horizons are best sampled by the laborious method of digging a pit, preparing a fresh vertical face, and carefully removing sampling units at suitable depths with a trowel, knife, or other instrument.

*Preparation of Samples.*—The soil sample should be placed in a noncontaminating container. Closely woven cloth sacks are convenient for this purpose. As soon as possible after collecting, spread the sample on a sheet of heavy paper in a room free of dust or chemical fumes for air-drying.<sup>5</sup> Break up any large clumps or clods to hasten the drying process. When dry, pass the soil through a sieve with openings 2 mm. in diameter. Place the material that fails to pass the sieve on a clean, hard surface, and crush with a hardwood roller or rubber-tipped pestle, using gentle to moderate pressure. It is unnecessary and undesirable to reduce rock fragments or coarse vegetative remains to 2-mm. size, but the crushing and sieving should continue until all primary particles smaller than 2 mm. in diameter have passed the sieve. Thoroughly mix the sieved sample, reduce by quartering or other suitable means, and store the stock sample so prepared in a closed glass container.<sup>6</sup>

The stock sample is used directly for many different chemical determinations, but certain procedures call for a sample of finer dimensions. To prepare a finely-ground sample,<sup>7</sup> place a small quantity of the stock sample in an agate mortar, and carefully crush until the entire sample has passed a nylon screen or silk bolting cloth containing 100 meshes to the linear inch. This process differs from the preparation of the stock sample in that primary mineral grains must be reduced in size and are not discarded. Great care must be taken in taking subsamples from the stock sample for chemical analysis, or for further grinding, because of the tendency for soil particles of different sizes to segregate. This may result in large subsampling errors, because the chemical nature of the larger primary particles (sand fraction) is usually quite different from that of the silt and clay particles.

Special precautions should be taken with samples intended for the determination of trace constituents. Ordinary paper bags fitted with plastic (polyethylene) liners are suggested for field collection and transportation of samples to the laboratory.

<sup>4</sup> Cline, Soil Sci., 58, 275-88, 1944. See also Jackson, Soil Chemical Analysis, 15-6 and 22-3.

<sup>5</sup> Ammonia fumes are a common source of contamination.

<sup>6</sup> In the procedures that follow, the stock sample will be referred to as "2-mm. soil."

<sup>7</sup> The finely-ground sample will be referred to as "100-mesh soil."

The samples can be dried on sheets of plastic and sieved through screens of nylon or similar material

## FIELD DESCRIPTIONS OF SOILS

The *Soil Survey Manual* should be consulted for detailed instructions for describing soils as they occur in place in the field<sup>8</sup>. Descriptions may include the following general headings: land form, relief, and drainage; parent material; the soil profile; stoniness; erosion or truncation; vegetation; and land use. In describing soil profiles, horizon boundaries are located with respect to depth and thickness. Description of individual horizons includes estimations of color, texture, structure, porosity, consistence, and other properties.

## PHYSICAL ANALYSIS OF SOILS

**Particle Size Distribution (Mechanical Analysis)**—The determination of the amounts of primary soil particles (sand, silt, and clay) is usually carried out by the pipet method<sup>9</sup> or by the hydrometer method<sup>10</sup> following removal of the soil or organic matter and the complete dispersion of the sample. The hydrometer method is rapid but the pipet method is considered to be more accurate. Data obtained for the percentages of clay, silt, and the various grades of sand are used to apply specific textural class names to the soil (clay loam, silt loam, loamy fine sand, etc.)<sup>11</sup>.

**Soil Moisture**—The total moisture content is determined by drying a weighed subsample to constant weight at 105°C. Unless the sample is air dry and finely ground, it is desirable to use a subsample of at least 25 g. The moisture content is expressed as a percentage of the oven-dry weight. The quantity of water a soil will hold under specified conditions in the field and in the laboratory is frequently of great practical and theoretical importance. Methods of measuring these soil moisture constants have been reviewed by Veihmeyer and Hendrickson<sup>1</sup>. Richards has discussed methods of measuring soil moisture tension<sup>12</sup>.

**Bulk Density and Particle Density**—The determination of bulk density also termed *volume weight* or *apparent density* poses the problem of obtaining an accurate measure of soil volume without compression or compaction. A number of techniques have been devised for this purpose<sup>13</sup>. Particle density is determined by the pycnometer method<sup>14</sup>.

**Soil Structure and Aeration**—Soil structure refers to the aggregation of primary particles which are separated from adjoining aggregates by surfaces of weakness.<sup>15</sup> The field description of soil structure is uncomplicated and includes estimation of

<sup>8</sup> Soil Survey Staff, *Soil Survey Manual*, U. S. Dept. Agr. Handbook 18, Washington D. C. 1951.

<sup>9</sup> Kilmer and Alexander, *Soil Sci.* 68, 15-24, 1949. See also Kilmer and Mullins, *Soil Sci.* 77, 437-41, 1954.

<sup>10</sup> Bouyoucos, *Soil Sci.* 38, 335-45, 1934. See also *Standard Specifications for Highways Materials and Methods of Sampling and Testing*, Pt. II, American Association of State Highway Officials, Washington D. C. 156-65, 1942.

<sup>11</sup> *Soil Survey Manual*, 205-23.

<sup>12</sup> *Soil Sci.* 68, 75-94, 1949. See also Richards, L. A. et al., *Diagnosis and Improvement of Saline and Alkali Soils*, U. S. Dept. Agr. Handbook 60, Washington D. C. 10, 20, 1954.

<sup>13</sup> *Soil Sci.* 68, 95-112, 1949.

<sup>14</sup> See Russell, *Soil Sci.* 68, 25-30, 1949.

<sup>15</sup> *Diagnosis and Improvement of Saline and Alkali Soils*, 122.

<sup>16</sup> *Soil Survey Manual*, 225.



the shape, size, and distinctness of aggregates. Laboratory measurements require an undisturbed sample, however, so that special precautions must be taken to ensure this. Soil samples prepared for chemical analysis are not suitable. Direct laboratory measurements of structure include determinations of aggregate-size distribution and aggregate stability. The movement and distribution of moisture and air in the soil is related to the size and arrangement of the soil pore space, which in turn is a function of structure. Therefore, laboratory measurement of such properties as total porosity and pore-size distribution are important in describing the structural condition of the soil and its suitability as a medium for plant growth. Various laboratory methods for measuring soil structure, including aggregate-size distribution and porosity and aeration, have been reviewed by Russell.<sup>17</sup>

## CARBONATE CARBON, ORGANIC CARBON, AND ORGANIC MATTER

### CARBONATE CARBON

#### *METHOD OF HUTCHINSON AND MACLENNAN*<sup>18</sup>

Carbon occurs in soil in inorganic and organic forms. The former usually consists of the carbonates of calcium or magnesium, although carbonates of the alkali metals are sometimes found in certain soils of the arid regions. Carbonate carbon is ordinarily reported as calcium carbonate equivalent. Rapid, approximate methods of determination include manometric procedures and acid neutralization.<sup>19</sup> Several methods for the more precise determination of carbonates are available.<sup>20</sup> The one given below requires a less elaborate experimental set-up than most.

*Procedure.*—Place 0.5 to 25 g. of 100-mesh soil (depending upon the carbonate content) in a 150-ml., round-bottom flask. Close the flask with a well-fitting 2-hole rubber stopper fitted to a separatory funnel, the stem of which extends well into the flask. Connect the flask to the side arm of a 1-liter filter flask with a drying tube partly filled with glass wool. Add exactly 50 ml. of carbonate-free 0.1 *N* sodium hydroxide, and 4 to 5 drops of thymolphthalein indicator<sup>21</sup> to the filter flask. Close the filter flask with a well-fitting, 1-hole rubber stopper, and connect to a good source of vacuum with a tube containing a glass stopcock. Evacuate the system, and then close the stopcock of the vacuum line. Add about 50 ml. of 0.6 *N* hydrochloric acid<sup>22</sup> to the separatory funnel, and slowly run the acid into the round-bottom flask, proceeding very carefully at first. Stop the flow of acid when a few drops remain in the funnel. After the acid has been in contact with the soil for a few minutes, gently shake the flask. Repeat the shaking 4 or 5 times over an interval of 20 min. Connect the top of the separatory funnel to a gas

<sup>17</sup> Soil Sci., 68, 25–35, 1949. See also Diagnosis and Improvement of Saline and Alkali Soils, 120–26.

<sup>18</sup> Hutchinson and MacLennan, Jour. Agr. Sci., 6, 323–27, 1914; Williams, 22, 838–44, 1932; Piper, C. S., Soil and Plant Analysis, The Hassell Press, Adelaide, Australia, 130–2, 1942.

<sup>19</sup> Soil and Plant Analysis, 128–36.

<sup>20</sup> Schollenberger, Soil Sci., 59, 57–63, 1945; Association of Official Agricultural Chemists, Methods of Analysis, 8th Ed., AOAC, Washington, D. C., 28–30, 1955.

<sup>21</sup> Dissolve 0.5 g. of thymolphthalein in 50 ml. of ethanol, and add 50 ml. of water.

<sup>22</sup> For soils containing manganese dioxide or much organic matter, add 1.5 g. of ferrous chloride ( $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ ) to the 50-ml. portion of 0.6 *N* hydrochloric acid immediately before use.

measurement of loss of ignition at 700°C. is sometimes used.<sup>29</sup> Organic matter may be determined directly and more precisely by treatment with hydrogen peroxide, but the method cannot be used in the presence of appreciable calcium carbonate or manganese dioxide.<sup>30</sup> Another procedure is to multiply the organic carbon from dry combustion by an empirical factor based on a mean carbon content of 58% for soil organic matter. Misleading values will be obtained on soil containing sources of elementary carbon, and on those in which the carbon content of the organic matter deviates appreciably from 58%. A number of methods have been developed based on the oxidation of organic matter by mixtures of chromic and sulfuric acid.<sup>31</sup> Provision for the elimination of chloride interference must be made, but the methods are not affected by calcium carbonate or elemental carbon. Empirical factors are used, but reasonably comparable estimates are given of the biologically active organic fraction of more or less closely related soils. The procedure given below is rapid and well-adapted to routine use.

**Reagent Solutions.** Potassium Dichromate, 1.0 *N*.—Dissolve 49.04 g. reagent grade  $K_2Cr_2O_7$  in water, and dilute to 1 liter.

Ferrous Sulfate, 0.5 *N*.—Dissolve 140 g. reagent grade  $FeSO_4 \cdot 7H_2O$  in water, add 40 ml. concentrated sulfuric acid, cool, and dilute to 1 liter. Standardize daily by titrating against 10 ml. of 1.0 *N* potassium dichromate as directed below.

Indicator.—Dissolve 0.16 g. of barium diphenylaminesulfonate in 100 ml. of water.

**Procedure.**—Weigh sufficient 100-mesh soil to provide 10 to 25 mg. organic carbon, and transfer to a 500-ml. conical flask. Add 10 ml. of 1.0 *N* potassium dichromate solution. Add rapidly 20 ml. of concentrated sulfuric acid, directing the stream into the solution, and immediately swirl the flask by hand for 1 min. Then let the flask stand on a sheet of asbestos for 30 min. Dilute with 200 ml. of water, add 10 ml. of 85% phosphoric acid, and 0.5 ml. of indicator solution. Titrate with ferrous sulfate solution to a light green end point. The end point is very sharp. If it is over-run, restore an excess of dichromate, and complete the titration by dropwise addition of ferrous sulfate solution. If more than 8 ml. of potassium dichromate solution are reduced, repeat the determination with less soil. Chlorides interfere but may be removed by prior leaching of the sample with water or by addition of silver sulfate to the sulfuric acid.<sup>32</sup>

Calculation.—

$$\frac{1 \text{ N } K_2Cr_2O_7 \text{ reduced, milliliters} \times 0.69}{\text{weight of sample, grams}} = \text{organic matter, per cent}$$

## TOTAL NITROGEN, AMMONIA, AND NITRATES

### TOTAL NITROGEN

#### KJELDAHL METHOD<sup>33</sup>

It is necessary to use finely ground soil to insure complete liberation of nitrogen from soils of high clay content,<sup>34</sup> and to prevent bumping during the distillation

<sup>29</sup> U. S. Dept. Agr. Circ. 139, 6-7, and 15.

<sup>30</sup> Robinson, Jour. Agr. Research, 34, 339-56, 1927.

<sup>31</sup> Schollenberger, Soil Sci., 59, 53-6, 1945.

<sup>32</sup> Soil Chemical Analysis, 215.

<sup>33</sup> Prince, Soil Sci., 59, 47-52; 1945. Adapted by permission.

<sup>34</sup> Walkley, Jour. Agr. Sci., 25, 598-609, 1935.

step with soils of high sand content. The method is not usually modified to include nitrate nitrogen since nitrates ordinarily comprise a small proportion of the total soil nitrogen. Nitrates are usually determined separately by the phenoldisulfonic acid method (see p 2317 below).

In the procedure given below mercury is used as a catalyst and sodium sulfate is added to raise the temperature of digestion. Catalysts or catalyst mixtures containing selenium are also commonly employed<sup>36</sup> and various modifications for shortening the period of digestion have been proposed<sup>36</sup>.

**Reagent Solutions** Sodium Hydroxide Potassium Sulfide—Dissolve 450 g of solid sodium hydroxide in 1 liter of water containing 12 g of potassium sulfide.

Boric Acid—Dissolve 40 g of boric acid in 1 liter of water.

Mixed Indicator—Mix 10 ml of 0.1% bromocresol green in 95% ethanol with 2 ml of 0.1% methyl red in 95% ethanol.

**Procedure**—Place 10 g of 100 mesh soil (use smaller quantity for soil high in organic matter) in a 650 ml Kjeldahl flask. Add 30 ml of concentrated sulfuric acid, 0.7 g of mercuric oxide (or 0.65 g of mercury) and 5 to 10 g of anhydrous sodium sulfate. Begin the digestion at low heat gradually increasing until organic matter has been destroyed and the solution has cleared in a total digestion period of about 2 hr. Excessively high digestion temperatures may result in a wasteful loss of sulfuric acid in the early stages and loss of ammonia in the later stages. Cool the flask, add 250 ml of distilled water and again cool. Add an excess (about 100 ml) of sodium hydroxide potassium sulfide solution and immediately join the flask to the condenser by means of a Kjeldahl connecting bulb. Mix the contents of the flask by shaking and collect about 150 ml of distillate in a receiving flask containing 25 to 50 ml of boric acid solution.<sup>37</sup> During the early and middle stages of the distillation the tip of the condenser tube should extend below the surface of the liquid in the receiving flask. Titrate the ammonia in the receiving flask with standard sulfuric or hydrochloric acid using 4 drops of mixed indicator. At the end point the blue color just disappears. One drop in excess turns the solution pink. Run a blank determination through the entire procedure substituting 0.2 g of sucrose for the soil.

**Calculation**—

$$\frac{\text{Net sample titer (milliliters)} \times \text{normality of standard acid} \times 1.4}{\text{weight of sample (grams)}} = \text{Nitrogen per cent}$$

## AMMONIA

### McLEAN AND ROBINSON METHOD<sup>38</sup>

Ammonia is a very labile compound in soil and must be determined immediately after sampling or as soon as possible after rapid oven drying at a temperature not in excess of 55°C. The ammonium ion is held by the negatively charged colloidal surfaces of the soil. It may be displaced by leaching the soil with a salt solution.

<sup>36</sup> Soil and Plant Analysis 200. Soil Chemical Analysis 185-6.

<sup>36</sup> Stubbsfield and DeTurk. Ind. Eng. Chem. Anal. Ed. 12, 396-9, 1940. Pepkowitz et al. 14, 856-7, 1942.

<sup>37</sup> Ammonia may also be absorbed in a measured quantity of dilute acid and the excess acid back titrated with standard alkali.

<sup>38</sup> McLean and Robinson. Jour. Agr. Sci. 14, 548-54, 1924. Prince. Soil Sci. 59, 47-59, 1915.

and determined by distillation and titration or by nesslerization. Soils may not be directly treated with alkali and the ammonia distilled, because of the danger of releasing ammonia from decomposition of organic components. Soils may be so treated and aerated at room temperature<sup>39</sup> but the technique presents difficulties.

**Procedure.**—Place 25 g. of 2-mm. soil in a 400-ml. beaker. If soil is not dry, weigh out another sample for moisture determination. Add 100 ml. of cold, normal sodium chloride solution.<sup>40</sup> Stir and let stand for 30 min. Decant the liquid through an 18.5-cm. Whatman No. 44 filter. Wash the soil with normal sodium chloride solution once by decantation, and then transfer it completely to the filter. Continue the leaching until the filtrate volume approximates 500 ml. Transfer to a distillation flask, add 3 to 4 g. of magnesium oxide and a small piece of paraffin, and distill the filtrate into a measured volume (10 to 15 ml.) of 0.02 *N* hydrochloric acid. Collect about 150 ml. of distillate, and titrate the excess acid with standard 0.02 *N* sodium hydroxide, using bromcresol green indicator. The end point is reached when the color of the indicator matches that in a reference buffer solution of pH 4.7 to 4.8, containing the same quantity of indicator.<sup>41</sup> Carry a reagent blank through the entire procedure.

Calculation.—

$$\frac{(\text{Blank titer, milliliters} - \text{sample titer milliliters}) \times \text{normality of HCl} \times 14,000}{\text{weight of sample, grams}} \\ = \text{Ammonium nitrogen (as } N), \text{ parts per million}$$

## NITRATE NITROGEN

### PHENOLDISULFONIC ACID METHOD<sup>42</sup>

The nitrate content of soil is subject to change, particularly under conditions of warm, moist storage. The determination should be made as soon as possible after the sample is collected. Nitrate is readily removed by leaching the soil with water. Nitrate in the extract may then either be reduced to ammonia and distilled,<sup>43</sup> or it may be directly determined photometrically. The former method is generally applicable to extracts of all types of soil, but the latter method is better suited to routine use. Phenoldisulfonic acid is the most widely used of the colorimetric reagents but precautions are needed for soils containing appreciable chlorides or those giving extracts colored with organic matter.

**Reagent Solutions.** Copper Sulfate.—Dilute 20 ml. of 1 *N* copper sulfate to 1 liter. This solution should be modified to include an additional 100 ml. of 0.6% silver sulfate solution, if the soil contains more than 10 p. p. m. chloride.

**Phenoldisulfonic Acid.**—Dissolve 25 g. of pure white phenol in 150 ml. of concentrated sulfuric acid. Add 75 ml. of fuming sulfuric acid (13 to 15% sulfur

<sup>39</sup> Matthews, Jour. Agr. Sci., 10, 72–85, 1920.

<sup>40</sup> Use 15% sodium chloride solution for soils of high ammonia content. Extraction with acidified salt solution is convenient with neutral and acid soils, but this method is not recommended for calcareous soils. See Piper, S. S., Soil and Plant Analysis, 205.

<sup>41</sup> Ammonia may also be determined by nesslerization of an aliquot of the distillate as directed under "Cation Exchange Capacity," p. 2328.

<sup>42</sup> Jackson, M. L., Soil Chemical Analysis, Prentice-Hall, Inc., Englewood Cliffs, N. J., 1958, 197–201. Adapted by permission.

<sup>43</sup> Soil and Plant Analysis, 206–7.

trioxide), and heat in a boiling water bath for 2 hr. Store in a glass-stoppered brown bottle.

**Standard Nitrate**—Dissolve 0.722 g of pure potassium nitrate in water, and dilute to the mark in a volumetric flask of 1 liter capacity. Prepare a permanent working standard by placing 50 ml in a porcelain dish and evaporating to dryness on a steam bath. When cool, add 3 ml of phenoldisulfonic acid solution, and mix at once, using a glass stirring rod with a flattened tip. After 10 min., dilute with water and make to 500 ml in a volumetric flask. One ml of the working standard contains 0.010 mg of nitrogen in nitrate form.

**Procedure**—Place 50 g of 2 mm soil in a 500 ml conical flask. If soil is not dry, weigh out another sample for moisture determination. Add 250 ml of copper sulfate extracting solution<sup>44</sup> and shake for 10 min. Allow the suspension to settle for a few minutes and then decant about 150 ml of the supernatant liquid into another flask containing 0.2 g of calcium hydroxide and 0.5 g of magnesium carbonate. Shake for 5 min., and filter on a dry filter, discarding the first 20 ml of filtrate. Transfer an aliquot to a porcelain dish and evaporate to dryness on a steam bath. When cool, add 3 ml of phenoldisulfonic acid solution, and mix at once using a glass stirring rod with a flattened tip. After 10 min., add about 15 ml of water and mix. When cool, add 1 l ammonium hydroxide solution slowly with stirring, until the yellow nitrophenoldisulfonic acid color develops. Then add a few milliliters in excess. Make the solutions to a suitable volume, and determine the percentage of transmission at a 420 mμ light maximum. Run a reagent blank through the entire procedure. Prepare a calibration curve by adding 1 l ammonium hydroxide solution to aliquots of the working standard, diluting to volume and measuring the percentage of transmission as above.

**Calculation**—

$$\frac{\text{Net nitrogen in aliquot, milligrams} \times 250,000}{\text{aliquot, milliliters} \times \text{weight of sample, grams}}$$

$$= \text{nitrate nitrogen (as } N), \text{ parts per million}$$

## TOTAL DETERMINATION OF MAJOR SOIL CONSTITUENTS BY FUSION ANALYSIS

The determination of the total quantity of certain soil constituents is usually carried out following fusion with various fluxes. The methods commonly used are based upon those developed for the analysis of minerals and rocks.<sup>45</sup> While mineral soils vary considerably in inorganic chemical composition, in most instances  $\text{SiO}_2$ ,  $\text{Al}_2\text{O}_3$ , and  $\text{Fe}_2\text{O}_3$  account for the major part of the soil mass. Other constituents such as  $\text{TiO}_2$ ,  $\text{CaO}$ ,  $\text{MgO}$ ,  $\text{K}_2\text{O}$ , and  $\text{Na}_2\text{O}$  sometimes occur in quantities greater than 1%. The total quantity of these constituents is of interest to students of soil mineralogy and soil genesis but is sometimes of very limited usefulness in considerations of soil fertility. This arises because the major portion of an element may occur in mineralogical forms that render it inaccessible to the plant root. For

<sup>44</sup> Prince (Soil Sci., 59, 47-52, 1915) extracts the soil with water in the presence of calcium oxide. Any organic matter in the extract is destroyed with nitrate free 30% hydrogen peroxide.

<sup>45</sup> Hillebrand and Lundell, *Applied Inorganic Analysis*, John Wiley and Sons, Inc., New York, 1929. See Corey and Jackson, *Anal. Chem.* 25, 624-8, 1953, for a semi-microchemical system of silicate analysis.

methods of measuring the quantity of an element capable of participating in plant nutrition, see "Chemical Analysis as a Measure of Soil Fertility," p. 2333. Many other constituents are normally found in trace quantities in soil; still others are of occasional occurrence; some play important roles in plant and animal nutrition and, in the absence of more refined techniques, total analysis may provide the only clue to the status of the soil with respect to them.

The selection of methods for inclusion in this section has been made with the foregoing considerations in mind. For example, methods for silica and for the combined oxides of iron, aluminum, and titanium are given because these constituents, in the form of oxides and silicates, comprise most of the inorganic portion of the soil. Methods for the total analysis of certain other elements are not given when the uses of such data were deemed rather narrowly specialized in nature. However, references are given to established methods for the total determination of constituents not represented by detailed procedures. For methods of determining the total quantity of biologically important trace constituents, some of which employ the fusion technique, see "Total Determination of Other Soil Constituents," p. 2322.

### SILICA AND TOTAL COMBINED OXIDES OF IRON, ALUMINUM, AND TITANIUM <sup>46</sup>

The fusion of the finely-ground soil sample is preceded by determinations of moisture content and loss on ignition. Results are expressed on the oven-dry basis because the absorbed water content of an air-dry soil sample varies slightly with atmospheric conditions. Sodium carbonate is the commonly employed flux. The total combined oxides of iron, aluminum, and titanium are determined in an aliquot of the filtrate from the silica determination. The combined oxide residue includes oxides of many other elements but the quantity of these in soils is usually very small in relation to iron oxide, titania, and alumina.

#### MOISTURE CONTENT (ABSORBED WATER)

*Procedure.*—Place 2 g. of 100-mesh soil in a wide-mouthed weighing bottle, and heat overnight in an oven at 110°C. Cool in a desiccator and weigh.

*Calculation.*—

$$\frac{\text{Loss in weight, grams} \times 100}{\text{oven-dry weight, grams}} = \text{moisture content, per cent}$$

#### LOSS ON IGNITION

The loss in weight between 100°C. and 700°C. roughly approximates the organic matter content of very sandy soils, but it also includes combined water which may be appreciable in soils of high clay content.

<sup>46</sup> AOAC, Methods of Analysis, 28–31; Bear, F. E., et al., Chemistry of the Soil, Reinhold Publishing Corp., New York, 329–30 and 334–6, 1955. Adapted by permission. If separate determinations of iron, aluminum, and titanium are desired, Robinson's detailed procedures should be consulted: U. S. Dept. Agr. Circ. 139, Washington, D. C., 1939; Soil Sci., 59, 7–11, 1915.

The total TiO<sub>2</sub> content of most soils approximates 1%, but in some tropical soils, the content may be much greater, and a considerable proportion of this may be included in the silica determination unless Robinson's procedures are followed.

**Procedure**—Place the residue from the determination of moisture content in a platinum dish and heat slowly in an electric furnace to 700°C and hold there 30 min. Cool in a desiccator and weigh.

**Calculation**—

$$\frac{\text{Loss in weight, grams} \times 100}{\text{oven dry weight grams}} = \text{loss on ignition, per cent}$$

### SODIUM CARBONATE FUSION

**Procedure**—Place the residue from the determination of loss on ignition in a 30 ml platinum crucible. Mix the residue with 5 times its weight of pure anhydrous sodium carbonate. Cover the crucible and heat at low redness until fusion begins, then increase heat to clear quiet fusion and finally give full heat of Meker burner for 20 min with flame oblique. Cool and detach the melt into a 250 ml porcelain dish. Add 100 ml of water and digest to disintegration on a steam bath. Slowly add 50 ml of concentrated hydrochloric acid with a cover over the dish and digest for 15 min. Wash the cover evaporate to dryness on a steam bath and bake until the residue is crisp.

### SILICA

**Procedure**—Add 10 ml of concentrated hydrochloric acid to the baked residue from the sodium carbonate fusion and then add 40 ml of hot water. Cover the dish and digest on the steam bath for about 15 min. Filter and wash with hot water containing 5 ml of concentrated hydrochloric acid per liter. Wash several times after all yellow color has disappeared from the silica. Place the filtrate and washings in a 400 ml beaker evaporate to dryness on a steam bath and bake until the residue has a crystalline appearance. Add 5 ml of concentrated hydrochloric acid and 40 ml of hot water and again digest filter and wash. Save the filtrate for subsequent determinations. Place the 2 silica residues with their filter papers in a previously ignited and weighed porcelain crucible. Moisten with a few drops of a saturated ammonium nitrate solution and heat cautiously with a low flame until the filter paper is charred. Gradually increase the heat and complete the ignition to constant weight by using a blast lamp or by placing the crucible in an electric furnace at 900°C. Cool in a desiccator and weigh.

**Calculation**—

$$\frac{\text{Weight of residue, grams} \times 100}{\text{oven dry weight of sample grams}} = \text{silica (as SiO}_2\text{), per cent}$$

### COMBINED OXIDES OF IRON, ALUMINUM AND TITANIUM

**Procedure**—Transfer to a 400 ml beaker an aliquot of the combined silica filtrates equivalent to 1 g of soil and concentrate to a volume of about 100 ml. Neutralize with a 1 to 1 solution of ammonium hydroxide. Make very slightly acid with hydrochloric acid and heat nearly to boiling. Add ammonium hydroxide solution until precipitation is complete and only a faint odor of ammonia can be detected. Cover the beaker and boil the contents for 1 min. If necessary add ammonium hydroxide solution dropwise until a faint odor of ammonia can be detected. Filter at once using ashless filter paper. Wash several times with hot 2.5% ammonium nitrate solution. Place the paper and its contents in the original beaker. Add 5 ml of concentrated hydrochloric acid macerate the paper quickly

using a pair of stirring rods, then add 50 ml. of water, and heat. Reprecipitate with ammonium hydroxide solution, filter, and wash the precipitate with the hot ammonium nitrate solution as previously directed. Continue to wash until the precipitate is free of chlorides. Dry the precipitate, separate it from the filter, and ignite it in a previously weighed porcelain crucible using the flame of an ordinary burner. Ignite the filter paper separately, and add the residue to the precipitate. Place the crucible in a muffle furnace and complete the ignition at 800° to 900°C. Cool in a desiccator and weigh.

Calculation.—

$$\text{Precipitate, grams} \times 100 = \text{Fe}_2\text{O}_3 + \text{Al}_2\text{O}_3 + \text{TiO}_2, \text{ per cent}$$

### CALCIUM, MAGNESIUM, POTASSIUM, AND SODIUM

These are important elements because of their effect on the physico-chemical behavior of the soil, and the role they play in plant nutrition. Ordinarily, such properties are much more closely related to the quantity of calcium, magnesium, potassium, and sodium held as exchangeable cations<sup>47</sup> on the negatively charged colloidal surfaces of the soil than to the total amount present. Methods for exchangeable cations are given in "Exchangeable Cations and the Cation Exchange Capacity," below, p. 2325. Methods of total analysis for these elements will not be given here. Standard procedures have been published by Robinson<sup>48</sup> and are patterned on those developed for the analysis of silicate rocks.

### MANGANESE

The manganese content of soil varies from trace quantities to several per cent, the latter amounts sometimes occurring in soils of the tropics. Much of the total manganese is quite inert as far as availability to the plant is concerned, and the determination of the manganese fraction occurring as an exchangeable divalent cation is much more useful in consideration of soil fertility (see "Calcium and Magnesium," under "Exchangeable Cations and the Cation Exchange Capacity," below, p. 2326). The determination of total manganese may be accomplished by digestion of the soil with hydrofluoric and sulfuric acids, followed by colorimetric measurement upon oxidation with periodate.<sup>49</sup>

### SULFUR<sup>49</sup>

Most of the sulfur in the soil is associated with the organic matter except in some soils of the arid regions, which may contain accumulations of gypsum. (See "Gypsum and Water Soluble Salts in Saline and Alkaline Soils," p. 2331.) The following procedure employs fusion with sodium carbonate and sodium nitrate followed by precipitation and determination of sulfur as barium sulfate.

*Procedure.*—Mix 1 to 2 g. of 100-mesh soil with 5 times the weight of sodium carbonate and 0.2 or 0.3 g. of sodium nitrate. Place in a platinum crucible and fuse in an electric furnace.<sup>50</sup> After fusion, thoroughly disintegrate the melt with

<sup>47</sup> Soils of the arid regions may also contain appreciable quantities of these elements as free carbonates, sulfates, and chlorides. See "Carbonate Carbon, Organic Carbon, and Organic Matter," above, pp. 2313 and 2314, and "Gypsum and Water Soluble Salts in Saline and Alkaline Soils," below, p. 2331.

<sup>48</sup> U. S. Dept. Agr. Circ. 139; Soil Sci., 59, 7-11, 1945.

<sup>49</sup> Robinson, Soil Sci., 59, 7-11, 1945. Adapted by permission.

<sup>50</sup> Special precautions must be taken to avoid contamination by sulfur if the fusion is performed with a gas flame. See Hillebrand and Lundell, Applied Inorganic Analysis, 571.



water on the steam bath, preferably overnight. Filter, wash, and make up to 150 to 175 ml, if not already of this volume. Add enough hydrochloric acid, in excess of the quantity necessary to neutralize the sodium carbonate, to make the solution about 1% hydrochloric acid. Bring to a boil, and precipitate the sulfate with 10 ml of a 10% barium chloride solution, cool, pass through a small fine filter, and wash. Ignite at a low temperature, and weigh. Occasionally because of a long digestion or too large an excess of acid, the silica will gel. One of the 2 following procedures may be adopted, and should be used before the barium chloride is added. Remove the silica by evaporation and filtration, or remove it by precipitating the neutralized solution with ammonia. Treat ignited barium sulfate with a few drops of hydrofluoric and sulfuric acids, cautiously ignite, and weigh again. As the reagents used invariably contain some sulfur, run blanks alongside and treat in the same manner as the determinations.

Calculation —

$$\frac{\text{Precipitate, grams} \times 0.343 \times 100}{\text{oven-dry weight of sample, grams}} = \text{sulfur (as SO}_3\text{), per cent}$$

## TOTAL DETERMINATION OF OTHER SOIL CONSTITUENTS

### PHOSPHORUS

Phosphorus plays essential roles in biological systems, and its determination in the soil has received much attention. A great many schemes have been proposed for obtaining phosphorus fractions that differ with respect to availability to the plant, but no general agreement exists as to which, if any, of these fractions represent well-defined components. (See the section on phosphorus below under

Chemical Analysis as a Measure of Soil Fertility, p 2334.) Several methods for determining total soil phosphorus have been proposed. A procedure consisting of perchloric acid digestion followed by colorimetric determination is given here because of its sensitivity and its adaptability to routine use. Its details are essentially those reported by Bray and Kurtz<sup>51</sup> except that the Gerritz modification of the molybdenum blue method is employed for color development.<sup>52</sup>

**Reagent Solutions** Quinaldine Red Indicator—Dissolve 0.01 g in 100 ml of water.

**Sodium Bisulfite.**—Dissolve 8 g of sodium bisulfite (meta, powder) in 100 ml of 0.5 M sulfuric acid. Prepare a fresh supply weekly.

**Molybdenum Blue.**—Place 19.5 g of MoO<sub>3</sub> (99.5 to 100%) in an 800 ml Kjeldahl flask, add 500 ml of concentrated sulfuric acid (18 M) and heat with gentle mixing until solution is complete. Cool to 150°C. Weigh, on a small watch glass 1.25 g of molybdenum metal powder (200 mesh, 99.5 to 100%) and transfer to the Kjeldahl flask. Keep at a temperature of 140° to 150°C, taking precautions not to exceed 150°C, and mix vigorously until the molybdenum metal is dissolved. The few

<sup>51</sup> Soil Sci., 59, 39-45, 1945. Adapted by permission. Other methods for total phosphorus are represented by that of Robinson, U. S. Dept. Agr. Circ. 139, 13-14, in which the soil is digested with hydrofluoric acid, and that of Muir, Analyst 77, 313-7, 1952, in which sodium carbonate fusion is used. Muir stated that incomplete recoveries of phosphorus are obtained with the perchloric acid digestion method. But Sherman and Eng. Chem., Anal. Ed., 14, 182-5, 1942, using the latter method, found that it gave better recoveries of phosphorus than those obtained by hydrofluoric acid digestion.

<sup>52</sup> Jour. Assoc. Off. Agr. Chem., 23, 321-34, 1940. U. S. Dept. Agr. Circ. 757, 3-4.

large particles that do not readily dissolve may remain. Cool, dilute a 5-ml. aliquot of this reagent with 20 ml. of water, and titrate with 0.1 *N*  $\text{KMnO}_4$  to a pink that persists for a minute. The reagent should be 0.11 *N*; if less than 0.109 *N*, add a calculated quantity of molybdenum, and dissolve by reheating in a Kjeldahl flask to 150°C. When stored in the dark in a Pyrex, glass-stoppered bottle, the reagent will keep indefinitely.

**Dilute Molybdenum Blue.**—Add 1 volume of molybdenum blue solution to 3 volumes of water and cool. Prepare freshly as needed.

**Standard Phosphate.**—Dissolve 0.2195 g. of pure dry  $\text{KH}_2\text{PO}_4$  in water, add 25 ml. of 0.5 *M* sulfuric acid, and dilute with water to 1 liter. This solution contains 50  $\mu\text{g}$ . of phosphorus per milliliter. Prepare working standards containing 10 and 1  $\mu\text{g}$ . of phosphorus per milliliter by appropriate dilution of the stock standard.

**Procedure.**—Place 1 g. of 100-mesh soil in a 100-ml. Kjeldahl flask, add 20 ml. of 60% perchloric acid, and digest until colorless or nearly so. Cool, dilute with water, and filter into a 250-ml. volumetric flask. Wash the residue well, make to the mark, and mix. Transfer an aliquot containing less than 50  $\mu\text{g}$ . of phosphorus to a 50-ml. volumetric flask. Add 1 drop of quinaldine red indicator, and adjust until just colorless with 1 *M* sodium carbonate and 1 *M* sulfuric acid. Bring to a total volume of 35 ml. with water, add 4 ml. of sodium bisulfite solution, and immerse in a boiling water bath for 40 min. Then add 2 ml. of dilute molybdenum blue reagent, and continue the heating for exactly 25 min. Cool in a pan of cold water, make to the mark, mix, and measure the transmittancy at 650  $\text{m}\mu$ . Run a blank determination through the entire procedure. Prepare a calibration curve by diluting aliquots of the working phosphorus standards to 35 ml., adding sodium bisulfite solution, and proceeding with color development as directed above.

**Calculation.**—

$$\frac{\text{Phosphorus in aliquot, micrograms} \times 250}{\text{aliquot, milliliters} \times \text{weight of sample, grams}} = \text{phosphorus, parts per million}$$

$$\text{Phosphorus, parts per million} \times 10^{-4} = \text{phosphorus, per cent}$$

$$\text{Phosphorus} \times 2.29 = \text{P}_2\text{O}_5$$

### BORON <sup>53</sup>

**Reagent Solutions.**<sup>54</sup> **Potassium Carbonate.**—Dissolve 40 g. of the anhydrous salt in 100 ml. of distilled water.

**Quinalizarin.**<sup>55</sup>—Dissolve 0.005 g. in 1 liter of 98.0% sulfuric acid.

**Standard Boron.**—Dissolve 2.857 g. of pure boric acid in distilled water, and dilute to 1 liter. This solution contains 0.5 mg. of boron per milliliter. Prepare working standards containing 10  $\mu\text{g}$ . and 1  $\mu\text{g}$ . of boron per milliliter by appropriate dilution of the stock standard.

**Procedure.**—Fuse 0.5 g. of 100-mesh soil with 3 g. of anhydrous sodium carbonate in a platinum crucible. Cool and place crucible in a 250-ml. beaker containing about 50 ml. of distilled water. Place a cover glass on the beaker and add 4 *N*

<sup>53</sup> Truog, *Soil Sci.*, 59, 85–90, 1945; AOAC, *Methods of Analysis*, 38. Adapted by permission.

<sup>54</sup> Ordinary soft-glass bottles and boron-free glassware should be used wherever possible to avoid possible contamination from borosilicate glass.

<sup>55</sup> MacDougall and Biggs (*Anal. Chem.*, 24, 566–9, 1952) found that increasing the quinalizarin concentration rendered the system much less sensitive to changes in sulfuric acid concentration.

sulfuric acid from time to time until the melt has disintegrated and the solution has a pH of 5.5 to 6.0 (use an external indicator). Transfer the solution to a 500 ml volumetric flask. Wash the beaker several times with water and add the washings to the flask not allowing the total volume to exceed 150 ml. Make to volume with methanol or ethanol and mix. Allow to stand and then decant through a filter or clarify by centrifuging. Place a 400 ml aliquot of the clear solution in a 600 ml beaker (boron free glass) and add 100 to 150 ml of water to prevent subsequent early precipitation. Add potassium carbonate solution until the solution is alkaline, evaporate to a small volume and transfer to a platinum dish. Evaporate to dryness and ignite at a temperature not over 450°C just long enough to destroy organic matter. After cooling add 4 ml of 0.36 N sulfuric acid and triturate thoroughly with a policeman. Place a 1 ml aliquot of this solution in a soft glass test tube (22 by 150 mm inside dimensions) add 10 ml of the quinalizarin sulfuric acid solution<sup>56</sup> stopper tube and mix thoroughly by swirling gently. Cool to 25°C transfer to a colorimeter tube<sup>5</sup> and read using a 590 to 610 mμ filter. Reagent blanks should be carried through the entire procedure.

A calibration curve is prepared by adding aliquots of the working standards containing from 0.2 to 3 μg of B to soft glass test tubes diluting to exactly 1 ml with water and proceeding with addition of the quinalizarin sulfuric acid solution and color measurement as directed above.

Calculation —

$$\frac{\text{Boron in aliquot, micrograms} \times 5}{\text{weight of sample, grams}} = \text{boron parts per million}$$

### COBALT, COPPER AND ZINC

A scheme of analysis for these elements in soils described by Holmes<sup>58</sup> employs perchloric acid digestion in a wide mouthed conical flask fitted with a special reflux cover glass. Dithizone is employed for the separations and the colorimetric estimations are made using the cobalt nitrosocresol, copper diethyldithiocarbamate and zinc dithizonate complexes. Holmes indicated complete removal of these elements by perchloric acid digestion when properly carried out. Other authorities<sup>59</sup> prefer to decompose the sample with hydrofluoric acid. Copper has been determined directly in soil digests without recourse to a preliminary dithizone separation using sodium diethyldithiocarbamate<sup>60</sup> or zinc dibenzylidithiocarbamate<sup>61</sup>.

<sup>56</sup> It is important that the final sulfuric acid concentration be exactly the same for all comparable determinations. Therefore the boron containing aqueous volume mixed with the 10 ml of quinalizarin sulfuric acid reagent must be exactly 1 ml and the reagent should be protected from contamination by atmospheric moisture. Convenient means for accomplishing the latter have been described (Soil Sci 59, 85-90 1945 Anal Chem 21 566-9 1942).

<sup>57</sup> The color comparison tubes must be selected with more than ordinary care to be free of imperfections or blemishes because of the high refractive index of the colored sulfuric acid solution.

<sup>58</sup> Holmes Soil Sci 59, 77-84 1945

<sup>59</sup> Soil Chemical Analysis 399 Prince in Chemistry of the Soil 342-9

<sup>60</sup> Soil Chemical Analysis 397-8

<sup>61</sup> Hagstrom and Rubins Storrs Agr Exp Sta Bul 360 1961

## DETERMINATION OF MOLYBDENUM

Molybdenum is determined by sodium carbonate fusion, followed by colorimetric estimation of the molybdenum-thiocyanate complex.<sup>62</sup> The molybdenum-dithiol complex has also been used.<sup>63</sup>

## OTHER CONSTITUENTS

Other constituents normally present in trace amounts in the soil, may sometimes occur in such quantities that plant or animal development is affected.<sup>64</sup> Two well-known examples of this are selenium and fluorine. Selenium is determined by the hydrobromic acid distillation method,<sup>65</sup> and fluorine by distillation and titration with thorium nitrate.<sup>66</sup>

## EXCHANGEABLE CATIONS AND THE CATION EXCHANGE CAPACITY

The colloidal portion of the soil consists of clay and humus. The surfaces of these substances have a negative charge that is neutralized by various cations held in exchangeable form. The total exchange capacity of a soil and the relative proportions among different cations absorbed on it may vary greatly from soil to soil. These variations affect the physical and chemical properties of soils and their suitability for growth of different crops.

## EXCHANGEABLE METAL CATIONS

The method depends upon the replacement of adsorbed cations by treatment with an excess of a single cation. This is followed by quantitative determination of the exchanged cations in the solution containing the excess of replacing ion. Many reagents have been used to accomplish this replacement.<sup>67</sup> Of these, neutral normal ammonium acetate is the most widely used.

AMMONIUM ACETATE EXTRACTION<sup>68</sup>

**Reagent Solution.** Neutral Normal Ammonium Acetate.—Prepare a solution containing 70 ml. of ammonium hydroxide (sp. gr. 0.90) and 58 ml. of acetic acid (99.5%) per liter of final solution desired. Cool, adjust exactly to pH 7.0, and dilute to volume with water.

**Procedure.**—Place 50 g. of 2-mm. soil in a 250-ml. conical flask, and add 100 ml. of ammonium acetate solution. Stopper, shake the flask for several minutes, and allow to stand overnight. Transfer the contents of the flask to a small Büchner funnel (Coors No. 1) fitted with moist 5.5-cm. Whatman No. 42 filter paper, and filter, applying gentle suction. Leach the soil with an additional 400 ml. of ammonium acetate, adding small portions at a time and using gentle suction, so that the leaching process will require not less than 1 hr. If desired, reserve the

<sup>62</sup> Purvis and Peterson, *Soil Sci.*, 81, 223-8, 1956.

<sup>63</sup> Clark and Axley, *Anal. Chem.*, 27, 2000-3, 1955.

<sup>64</sup> McMurtrey and Robinson, in *Soils and Men*, U. S. Dept. Agr. Yearbook of Agriculture, Washington, D. C., 807-29, 1938. See also Bear, in *Soil*, U. S. Dept. Agr. Yearbook of Agriculture, 165-71, 1957.

<sup>65</sup> Robinson, *Soil Sci.*, 59, 93-5, 1945; *Methods of Analysis*, 36-8.

<sup>66</sup> McIntire, *Soil Sci.*, 59, 105-9, 1945; *Methods of Analysis*, 39.

<sup>67</sup> Kelley, *Cation Exchange in Soils*, Reinhold Publishing Corp., New York, 83-95, 1948.

<sup>68</sup> U. S. Dept. Agr. Circ. 757, 7-9.

cations in soils of the arid regions containing alkaline earth carbonates or soluble alkali salts.<sup>76</sup>

### CATION EXCHANGE CAPACITY

The determination of cation exchange capacity depends upon the saturation of the negatively charged soil colloids with a particular cation, followed by the quantitative replacement and determination of the saturating ion. Because of the complex and variable nature of the soil colloidal fraction, it may be impossible to define precisely a set of experimental conditions by which this can be achieved for all soils. In practice, one of several more or less arbitrary methods is employed. The results obtained by a given method have practical value when comparing a given soil with other more or less closely related soils. The procedure given here is widely used but it is only one of several methods.<sup>77</sup> In the method given below,<sup>78</sup> the soil is saturated with ammonium ion, which is then displaced with acidified sodium chloride, and determined.

#### EXTRACTION OF ADSORBED AMMONIA

**Reagent Solution.** Acidified Sodium Chloride.—Dissolve 100 g. of ammonia-free sodium chloride in 1 liter of approximately 0.005 *N* hydrochloric acid.

**Procedure.**—Saturate the soil with ammonium ion by treatment with ammonium acetate solution as directed under "Ammonium Acetate Extraction," p. 2325, above. Wash out the excess of ammonium acetate from the ammonium-saturated soil on the Büchner funnel with 200 ml. of 95% ethanol,<sup>79</sup> using small portions at a time and draining well between each addition. Then extract<sup>80</sup> the adsorbed ammonium by leaching the soil with 450 ml. of acidified sodium chloride solution, adding small portions at a time and draining well between each addition. Determine ammonia in the extract by distillation or by nesslerization as directed below.

#### AMMONIA BY DISTILLATION

**Procedure.**—Transfer the sodium chloride extract to a Kjeldahl flask, add 25 ml. of 1 *N* sodium hydroxide, and distill 200 ml. into 60 ml. of standard 0.2 *N* sulfuric acid. Titrate the excess of acid with standard 0.1 *N* sodium hydroxide, using methyl red indicator. Run a blank determination on the acidified sodium chloride solution in the same manner.

**Calculation.**—

$$\frac{(\text{Blank titer, milliliters} - \text{sample titer, milliliters}) \times \text{normality of NaOH} \times 100}{\text{weight of sample, grams}}$$

= cation exchange capacity, milliequivalents per 100 g. of soil

<sup>76</sup> For a discussion of this problem, see Soil and Plant Analysis, 157-9. See also Bower, et al., Soil Sci., 73, 251-61, 1952.

<sup>77</sup> See Kelley, op. cit., 95-9.

<sup>78</sup> U. S. Dept. Agr. Circ. 757, 9-10.

<sup>79</sup> The alcohol should be tested for acidity. Not more than 0.01 milliequivalents of sodium hydroxide should be required to bring 50 ml. of 95% ethanol mixed with 35 ml. of carbon dioxide-free water to a slight pink color with phenolphthalein.

<sup>80</sup> With calcareous soils, there may be some loss of ammonia during the extraction. To avoid this, transfer the alcohol-washed soil and filter paper to a Kjeldahl flask, add 400 ml. of water, about 10 g. of sodium chloride, 5 drops of a 1:1 by volume mixture of mineral oil and capryl alcohol, and 25 ml. of normal soil hydroxide. Distil and determine ammonia as directed in the following section.

## AMMONIA BY NESSLERIZATION

**Reagent Solutions** **Nessler Reagent**—Dissolve 45.5 g of mercuric iodide and 35.0 g of potassium iodide in a minimum amount of water. Add 112 g of potassium hydroxide, mix, cool, and dilute to 1 liter with water. Allow to settle for a few days and use the clear supernatant liquid which should be stored in a brown glass bottle.

**Sodium Tartrate**—Dissolve 100 g of sodium tartrate ( $\text{Na}_2\text{C}_4\text{H}_4\text{O}_6 \cdot 2\text{H}_2\text{O}$ ) in water and dilute to 1 liter.

**Standard Ammonium**—Dissolve 2.674 g of ammonium chloride in water and dilute to the mark in a volumetric flask of 1 liter capacity. Add 1 ml of chloroform as a preservative. This solution contains 0.05 milliequivalent ammonium ion per milliliter.

**Procedure**—Transfer the sodium chloride extract to a 500 ml volumetric flask and make to volume with the sodium chloride extracting solution. After mixing, transfer an aliquot to a 50 ml volumetric flask and dilute to about 45 ml with water. Add 1 ml of sodium tartrate solution and 2.5 ml Nessler reagent, mixing well after each addition. Make to volume, mix, and measure percentage of transmission after 20 min at 410 m $\mu$  light maximum. Run a blank determination using a volume of sodium chloride extracting solution equal to the sample aliquot.

The calibration curve is prepared by adding sodium tartrate solution and Nessler reagent as directed above to aliquots of a working standard prepared by diluting 5 ml of the standard ammonium solution to 500 ml. The working standard contains 0.0005 milliequivalents ammonium ion per milliliter.

**Calculation**—

$$\frac{\text{Sample ammonia, milliequivalents} - \text{blank ammonia, milliequivalents} \times 500 \times 100}{\text{aliquot milliliters} \times \text{weight of sample grams}} \\ = \text{cation exchange capacity milliequivalents per 100 g of soil}$$

## DETERMINATION OF SOIL REACTION (pH), EXCHANGEABLE HYDROGEN, AND LIME REQUIREMENT

SOIL REACTION (pH VALUE)<sup>81</sup>

Soil reaction is best determined electrometrically using the glass electrode although methods employing indicator papers or solutions are useful for rough approximations. Practical inferences may be drawn relating soil reaction to chemical properties of the soil and its suitability for plant growth. (See Chemical Analysis as a Measure of Soil Fertility, p. 2333 below.) Many methods have been proposed for preparing soil samples for pH measurements with the glass electrode. Some soils of the arid regions present problems because of solubility and hydrolysis effects involving free alkali and alkaline earth salts<sup>82</sup>. High ratios of soil to water more closely approach field conditions but results are likely to be unreliable because of poor soil electrode contact and other effects<sup>83</sup>. Increasing ratios of water to soil are likely to increase pH values somewhat because of dilution effects. The

<sup>81</sup> See Reed and Cummings (Soil Sci. 59, 97-104, 1945) for a review of methods and techniques for measuring soil pH values.

<sup>82</sup> Diagnosis and Improvement of Saline and Alkali Soils, 17-8.

<sup>83</sup> Davis, Soil Sci. 56, 405-22, 1913.

choice of method, two of which are given below, is more or less arbitrary for most soils. There is probably no justification in reporting measurements with greater precision than the nearest 0.1 pH unit.

#### 1:1 SOIL:WATER RATIO METHOD <sup>84</sup>

*Procedure.*—Place about 20 g. of 2-mm. soil in a 50-ml. beaker. Add an equal volume of distilled water, and stir at regular intervals for 1 hr. Measure the pH value of the suspension with the glass electrode, stirring well just before placing the electrodes deep in the suspension.

#### SATURATED SOIL PASTE METHOD <sup>85</sup>

*Procedure.*—Place about 40 ml. of 2-mm soil in a 50-ml. beaker. Add water to the soil in small increments without stirring, until water just wets the entire soil mass. Slowly add a few drops more until the surface glistens slightly. Then stir with a glass rod, and add water dropwise until the soil forms a thin paste that slowly flows together to close a hole made by the rod. Insert the electrodes into the paste, and measure the pH value. Move the glass electrode about to insure good soil contact and record the pH value when the reading is sensibly constant.

### EXCHANGEABLE HYDROGEN

Exchangeable hydrogen may be determined directly or it may be determined by difference by deducting the sum of the exchangeable metallic cations from the cation exchange capacity. Since the magnitude of the latter value may vary somewhat with the method of determination (see "Cation Exchange Capacity," p. 2327, above), it follows that the value for exchangeable hydrogen is also empirical. Direct methods of determination depend upon the measurement of the hydrogen ion that is released when soil is treated with salt solutions that are well buffered in the neutral range. The replacing systems include those containing such cations as ammonium, barium, or calcium buffered with substances such as acetate, triethanolamine, or *p*-nitrophenol.<sup>86</sup> Values for exchangeable hydrogen obtained by various direct methods do not always agree closely among themselves, or with those for exchangeable hydrogen obtained by difference. As with any set of empirical methods, the particular method used must be specified when comparing results obtained on different soils. The practical usefulness of whichever method is adopted usually depends upon the correlation of the values obtained by a given method with some other set of values.

#### EXCHANGEABLE HYDROGEN BY DIFFERENCE <sup>87</sup>

*Calculation.*—Deduct the sum of the exchangeable metallic cations (see "Determination of Individual Metal Cations," above, p. 2326) (calcium, magnesium, manganese, potassium, and sodium), expressed as milliequivalents per 100 g. of soil, from the cation exchange capacity (see "Calculation," under "Ammonia by Nesslerization," above, p. 2328), expressed as milliequivalents per 100 g. of soil. Soils of the humid region usually contain such small quantities of exchangeable sodium that this value is often not considered in the calculation for such soils.

<sup>84</sup> U. S. Dept. Agr. Circ. 757, 5.

<sup>85</sup> Soil Chemical Analysis, 45-6.

<sup>86</sup> See the discussion by Peech and Bradfield, *Soil Sci.*, 65, 35-55, 1948.

<sup>87</sup> U. S. Dept. Agr. Circ. 757, 12.

### DIRECT DETERMINATION OF EXCHANGEABLE HYDROGEN<sup>88</sup> NEUTRAL CALCIUM ACETATE METHOD

This method is only one of several direct methods that have been proposed for this determination

**Reagent Solutions** Calcium Acetate, 0.5 M.—Dissolve 176 g  $\text{Ca}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot \text{H}_2\text{O}$  in 2 l of water, and adjust to pH 7 by titration with normal acetic acid, using the glass electrode as indicator (Approximately 4 ml of the acid are required) Prepare the supply needed for 1 week, and store in a bottle provided with a siphon and soda lime tube

**Barium Hydroxide, 0.1 N.**—Dissolve 0.05 molar weight  $\text{Ba}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$  per liter allowing 2% excess for impurities and  $\text{CO}_2$  contamination Let stand 24 hr Prepare a storage bottle, freed of  $\text{CO}_2$ , and provided with a siphon and soda lime guard tube Draw the barium hydroxide solution into the prepared bottle by applying suction at the soda lime tube and drawing the solution through a fitted glass filter Connect the solution with a 25 ml pinchcock buret, provided with a side tube for gravity feed and soda lime tube at top<sup>89</sup>

**Procedure.**—Place a weighed sample of 2 mm soil containing 1 to 2 milliequivalents of exchangeable hydrogen in a 250 ml conical flask Add about 100 ml of the calcium acetate solution stopper, and shake several times during the first hour Let stand overnight Filter the soil suspension through a 12.5 cm paper into a 250 ml volumetric flask Transfer the soil to the filter with a stream of the calcium acetate solution and wash with small quantities of this solution until volume is just below the 250 ml mark Discard the soil and make to volume with the same solution Transfer to a 400 ml beaker, rinse flask with water, and titrate potentiometrically with the barium hydroxide solution to pH 8.8 Similarly, titrate a 250 ml portion of the calcium acetate solution

**Calculation.**—

$$\frac{\left\{ \begin{array}{l} (\text{Soil extract titer, milliliters} - \text{calcium acetate titer, milliliters}) \\ \times \text{normality of Ba(OH)}_2 \times 100 \end{array} \right\}}{\text{weight of sample, grams}}$$

= exchangeable hydrogen, milliequivalents per 100 g of soil

### LIME REQUIREMENT<sup>90</sup>

This term is used to indicate the quantity of a liming material needed to adjust the reaction of an acid soil to some specified pH value, commonly 6.5 or 7.0 The term does not have a precise definition, and in using it, both the intended pH value and the particular liming material should be specified (i.e.,  $\text{CaCO}_3$ ,  $\text{CaO}$  etc.) Most methods for determining lime requirement involve the estimation of exchangeable hydrogen Since the laboratory methods do not allow for certain effects encountered in the field, it is necessary to multiply the laboratory results by an empirical "lime factor," which ranges, for various soils, from 1.5 or even less to as much as 3

<sup>88</sup> Methods of Analysis, 42-3 See also Shaw, Jour Assoc Off Agr Chem, 34, 595-7 1951, and 35, 597-621, 1952

<sup>89</sup> Standardize by titrating into a measured volume of standard hydrochloric acid Do not attempt to adjust to exactly 0.1 N See Treadwell and Hall, Analytical Chemistry II Quantitative, 7th Ed., John Wiley and Sons Inc., New York, 481-2, 1930

<sup>90</sup> Peech and Bradfield Soil Sci., 65, 35-55, 1948



## GYPSUM AND WATER SOLUBLE SALTS IN SALINE AND ALKALI SOILS

### DETERMINATION OF GYPSUM <sup>91</sup>

Considerable accumulations of gypsum <sup>92</sup> may occur in some soils of the arid regions. The method given below depends on the conductimetric estimation of gypsum separated from a soil-water extract by acetone precipitation. The method is simple and is more rapid than older procedures involving separate determinations of calcium and sulfate.

*Procedure.*—Place 10 to 20 g. of air-dry, 2-mm. soil <sup>93</sup> in an 8-oz. bottle, and add a measured volume of distilled water sufficient to dissolve the gypsum present.<sup>94</sup> Shake by hand 6 times at 15-min. intervals or agitate for 30 min. in a mechanical shaker. Filter the extract through paper of medium porosity. Transfer a 20-ml. aliquot of the filtered extract containing 0.1 to 0.6 milliequivalents of calcium sulfate to a 50-ml. conical centrifuge tube. Add 20 ml. of reagent grade acetone, and mix the contents of the tube. Let stand until the precipitate flocculates, usually 5 to 10 min. Centrifuge for 3 min. at 1000 times gravity, decant the supernatant liquid, invert the tube, and drain on filter paper for 5 min. Disperse the precipitate, and rinse the wall of the tube with a stream of 10 ml. of acetone blown from a pipet. Centrifuge for 3 min., decant, and drain for 5 min. as before. Add exactly 40 ml. of distilled water to the tube, stopper, and shake until the precipitate is completely dissolved. Measure the conductivity with a conductivity cell and Wheatstone bridge. Correct the conductivity reading to 25°C., using the formula: <sup>95</sup>

$$EC_{25} = EC_t [1 + 0.02 (25 - t)]$$

where  $EC_{25}$  and  $EC_t$  are the electrical conductivities at 25°C., and at the observed temperature,  $t$ , respectively. Calculate the concentration of calcium sulfate in solution from a graph prepared from the following data:

<i>CaSO<sub>4</sub> Concentration</i> (Milliequivalents per Liter)	<i>Electrical Conductivity</i> at 25°C. (Millimhos per Centimeter)
1	0.121
2	0.226
5	0.500
10	0.900
20	1.584
30.5	2.205

<sup>91</sup> Bower and Huss, *Soil Sci.*, 66, 199–204, 1948. Adapted by permission.

<sup>92</sup> Calcium carbonate is also a common constituent of such soils. For determination, see "Carbonate Carbon, Organic Carbon, and Organic Matter," above, p. 2313.

<sup>93</sup> The soil must not have been oven-dried. See Bower and Huss, *op. cit.*

<sup>94</sup> A 1:5 soil-water ratio will dissolve about 15 milliequivalents per 100 g. of soil. Use a more dilute extract than 1:5 if it is found that the gypsum content of the soil approaches 15 milliequivalents per 100 g.

<sup>95</sup> International Critical Tables, 1, 231 and 236.

Calculation.<sup>96</sup>—

$$\frac{\text{CaSO}_4 \text{ milliequivalents per liter} \times 0.2}{\text{soil, grams water, milliliters extraction ratio}}$$

= gypsum, milliequivalents per 100 g of soil

### WATER SOLUBLE SALTS

Excessive quantities of soluble salts may occur in some soils of the arid regions. The soluble ions usually present consist chiefly of sodium, calcium, magnesium chloride, and sulfate, although the potassium, bicarbonate, carbonate, and nitrate ions may sometimes occur in more than minor amounts.<sup>97</sup> High levels of soluble salts sometimes occur in soils of the humid regions that have been influenced by waters of marine origin or by very heavy applications of fertilizer. Various ratios of soil to water have been proposed for the extraction and estimation of soluble salts<sup>98</sup> but the composition of the extract obtained at high ratios of water to soil does not represent the conditions actually encountered by the crop in the field.<sup>99</sup> For general purposes, the U S Salinity Laboratory recommends extraction at the moisture saturation percentage, which is a rather easily reproduced moisture condition that can be approximated without special laboratory apparatus.

#### PREPARATION AND ANALYSIS OF THE SATURATION EXTRACT<sup>100</sup>

**Procedure.**—Add distilled water to a 250 g sample of 2 mm air-dry soil while stirring with a spatula. At saturation the soil paste glistens as it reflects light flows slightly when the container is tipped, and the paste slides freely and cleanly off the spatula for all soils but those with a high clay content. After mixing allow the sample to stand for 1 hr or more, and then the criteria for saturation should be rechecked. Free water should not collect on the soil surface, nor should the paste stiffen markedly or lose its glistening appearance on standing. If the paste does stiffen or lose its glisten, remix with more water. Transfer the saturated paste to a filter funnel, and filter under vacuum.<sup>101</sup> If the initial filtrate is turbid, refilter through the soil or discard.

The saturation extract so prepared may be analyzed for a variety of inorganic constituents, in addition to the determination of specific electrical conductance. The latter determination is particularly useful in diagnostic work dealing with crop growth on soils of the arid regions. The soluble cations and anions commonly determined in saline and alkali soils include calcium, magnesium, sodium, potassium, carbonate, bicarbonate, sulfate, and chloride.<sup>102</sup>

<sup>96</sup> The formula assumes a 20 ml aliquot of extract taken and the precipitate dissolved in 40 ml of water for conductivity reading.

<sup>97</sup> Diagnosis and Improvement of Saline and Alkali Soils, 3.

<sup>98</sup> Soil Chemical Analysis, 240-51.

<sup>99</sup> Reitemeier and Wilcox, *Soil Sci.*, 61, 281-93, 1946.

<sup>100</sup> See Diagnosis and Improvement of Saline and Alkali Soils, 84-100, and Magstad *et al.*, *Soil Sci.*, 59, 65-75, 1945, for details of preparation and analysis of saturation extracts.

<sup>101</sup> For chemical analysis, the saturated paste should stand 4 to 16 hr before extraction.

<sup>102</sup> For detailed procedures and interpretation of results, see Diagnosis and Improvement of Saline and Alkali Soils.

CHEMICAL ANALYSIS AS A MEASURE OF SOIL FERTILITY<sup>103</sup>

Methods of soil chemical analysis have found widespread use in the evaluation of the soil as a medium for crop growth. Such evaluation may apply to plant growth in general, or it may be geared to the individual needs of a specific crop. It must consider such direct effects as deficiency conditions in which the level of a biologically essential ion is so low that plant growth is limited, as well as toxicity conditions in which the level of an ion, biologically essential or not, is so high that the plant is adversely affected. The latter situation, perhaps, should be extended to include the nonspecific effects of high concentrations of soluble salts. Other determinations may be indirectly related to plant growth. For instance, certain crops are quite specific in their pH requirements. This may not be attributable to the effect of the hydrogen ion concentration *per se*, but to some other factor, known or unknown, that is correlated with pH value.

The total quantity of an element in the soil is not necessarily a reliable index of its availability to the plant. That portion of an element occurring as a constituent of soil minerals may contribute only very slowly to the portion actively participating in plant nutrition because of the limited rate of mineral weathering. This consideration does not apply so strictly to total analysis for elements such as nitrogen and sulfur that have reserve forms that are organic rather than inorganic in nature. Here the processes of organic decay can more rapidly convert the element into soluble ionic forms that can be utilized by plants, although the rate at which the conversion takes place varies with the rate of decomposition of the organic matter. In the case of some biologically important elements of trace or occasional occurrence in the soil, total analysis is sometimes used because better methods of establishing availability are lacking.

Early efforts to devise chemical techniques for determining the quantity of an element in the soil available to the plant were directed toward the duplication of the solvent action of plant roots. It is now recognized that the situation is far more involved than was at first realized, and that there is probably no simple, convenient way of simulating such effects in the laboratory. Methods that purport to remove and measure the fraction of an element available for plant growth are now recognized as empirical in nature. Their usefulness lies in the correlations that can be made between the values obtained and the actual behavior of a crop under various conditions in the field.

## AVAILABILITY OF CATIONS

For those elements that occur as cations in solution, the quantity held in exchangeable form on the cation exchange complex is probably the best single measure of availability. This represents a reasonably well-characterized fraction for potassium, calcium, magnesium, manganese,<sup>104</sup> and possibly for essential trace constituents, such as zinc and copper. Exception to this statement is found in those soils of the arid regions that contain accumulations of alkali and alkaline earth salts. It should also be pointed out that the presence of calcium as an exchange-

<sup>103</sup> See Bear, F. E., *et al.*, Diagnostic Techniques for Soils and Crops, The American Potash Institute, Washington, D. C., 1948, for a survey of chemical and biological approaches to this problem.

<sup>104</sup> The ammonium cation is frequently present in small quantities in soils. For determination, see "Ammonia," p. 2316, above.

able cation is especially significant from the standpoint of its predominant role in reducing soil acidity rather than from its role in plant nutrition. Symptoms of calcium deficiency in the plant are quite uncommon even in acid soils containing little exchangeable calcium.

### AVAILABILITY OF PHOSPHORUS

In contrast to the situation with cations there is no general mechanism for retention of inorganic anions in available forms in the soil. Such anions as nitrate<sup>1</sup> and chloride and sulfate<sup>106</sup> are readily removed by leaching. This does not apply to phosphorus, however, which occurs in available form as orthophosphate. The phosphate anion is held tenaciously by the soil but no general agreement exists as to the precise nature of the equilibria between phosphate available to the plant and the various mineral and organic reserve forms of phosphorus. Also there is no general agreement on the best chemical method of measuring phosphorus availability. The methods that follow represent 3 of the several approaches that have been made to the problem of devising a suitable extractant for available soil phosphorus.

#### DILUTE ACID SOLUBLE PHOSPHORUS— MODIFIED TRUOG METHOD<sup>10</sup>

This method is one of the many procedures that employ dilute mineral or organic acid solutions for extraction. It has been widely used on acid soils but on soils that are not acid or on those that have been fertilized with rock phosphate there has been poor correlation between the results obtained and crop response to phosphate fertilization.<sup>108</sup>

**Reagent Solution.** Sulfuric Acid Ammonium Sulfate Extractant—Dilute standard stock 0.1 N sulfuric acid to 0.002 N and add 3 g of ammonium sulfate per liter.

**Procedure.** Place 4 g of 2 mm soil in a 500 ml conical flask. Add 400 ml of the extractant solution, stopper and shake for 30 min in a reciprocating or end over end shaker. Filter it once through 11 cm Whatman No. 42 filter paper discarding the filtrate until it comes through perfectly clear. Transfer an aliquot to a 50 ml volumetric flask, dilute to 35 ml with distilled water and proceed with the color development and measurement as directed for determination of total phosphorus<sup>109</sup> beginning with the addition of the sodium bisulfite solution. (It is not necessary to adjust the acidity.)

**Calculation.**—

$$\frac{\text{Phosphorus in aliquot, micrograms} \times \text{extractant volume, milliliters}}{\text{aliquot milliliters} \times \text{weight of sample, grams}}$$

= dilute acid soluble phosphorus parts per million

#### ADSORBED PHOSPHORUS—FLUORIDE EXTRACTION METHOD<sup>110</sup>

In this method the fluoride ion is used to replace or dissolve phosphorus adsorbed or precipitated on the colloidal soil surfaces. The method appears to be

<sup>1</sup> See Nitrate Nitrogen, p. 2317 above for determination.

<sup>106</sup> See Water Soluble Salts, p. 2339 above.

<sup>107</sup> U. S. Dept. Agr. Circ. 707, 3-7.

<sup>108</sup> Soil Chemical Analysis, 1:4.

<sup>109</sup> See Phosphorus, p. 2322 above.

<sup>110</sup> Bray and Kurtz, Soil Sci. 59, 39-45, 1945.

adaptable to a wider range of soil conditions than are the dilute acid extraction methods.

**Reagent Solutions.** Ammonium Fluoride-Hydrochloric Acid Extractant.—Add 15 ml. of *N* ammonium fluoride <sup>111</sup> and 25 ml. of 0.5 *N* hydrochloric acid to 460 ml. of distilled water, to give a solution 0.03 *N*, with respect to ammonium fluoride, and 0.025 *N* with respect to hydrochloric acid.

**Stock Stannous Chloride.**—Dissolve 10 g. of reagent grade stannous chloride ( $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ ) in 25 ml. of concentrated hydrochloric acid. Store in a black, glass-stoppered bottle, and prepare fresh every 6 weeks.

**Ammonium Molybdate-Hydrochloric Acid.**—Dissolve 15 g. of reagent grade ammonium molybdate ( $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$ ) in about 350 ml. of warm distilled water (50°C.). Filter if necessary. Add 350 ml. of 10 *N* hydrochloric acid, slowly with stirring. Cool and dilute to 1 liter with distilled water. Mix and store in a black, glass-stoppered bottle. Prepare fresh every 2 months.

**Dilute Stannous Chloride.**—Add 1 ml. of stock stannous chloride solution to 332 ml. of distilled water, and mix. Prepare fresh every 4 hr. as needed.

**Procedure.**—Place 1 g. of 2-mm. soil in a glass vial. Add 7 ml. of ammonium fluoride-hydrochloric acid extractant, and shake for 1 min. Pour at once on a 7-cm. filter paper. To a 1-ml. aliquot of the filtrate, add 6 ml. of distilled water and 2 ml. of ammonium molybdate-hydrochloric acid reagent. Mix well. Add 1 ml. of dilute stannous chloride reagent and mix. After 5 or 6 min., read photometrically at 675  $\text{m}\mu$ . The standardization curve is prepared from graded amounts of standard phosphate solution developed in the same manner, including the same quantity of extractant solution.

**Calculation.**—

$$\frac{\text{Phosphorus in aliquot, micrograms} \times \text{extractant volume, milliliters}}{\text{aliquot, milliliters} \times \text{weight of sample, grams}}$$

= adsorbed phosphorus, parts per million

#### BICARBONATE EXTRACTABLE PHOSPHORUS <sup>112</sup>

This method was developed in an attempt to find a procedure for extracting available phosphorus that would be applicable to acid, neutral, and alkaline soils. On calcareous soils, the reagent is presumed to prevent secondary precipitation of phosphorus during extraction, by depression of the calcium ion activity. On acid and neutral soils, the phosphate adsorbed on the surface of the soil particles is presumed to be displaced by ionic competition with the bicarbonate, carbonate, and hydroxyl ions of the extracting solution.

**Reagent Solutions.** Sodium Bicarbonate Extractant.—Prepare a 0.5 *M* solution of sodium bicarbonate, adjusted to pH 8.5 with sodium hydroxide. Add a layer of mineral oil to prevent changes in pH during storage.

**Ammonium Molybdate-Hydrochloric Acid.**—Prepare as directed for the fluoride extraction method, above, except that each liter should contain 410 ml. of 10 *N* hydrochloric acid.

**Dilute Stannous Chloride.**—Prepare from stock stannous chloride solution as directed for the fluoride extraction method, above.

<sup>111</sup> The 1 *N* ammonium fluoride solution should be stored in a wax-lined bottle. The extractant solution will keep in glass for more than 1 year.

<sup>112</sup> Olsen, *et al.*, U. S. Dept. Agr. Circ. 939, Washington, D. C., 1954.

**Procedure**—Place 5 g of 2 mm soil in a suitable flask. Add 100 ml of sodium bicarbonate extractant solution and 1 teaspoon of carbon black<sup>113</sup>. Shake at a constant rate for 30 min. Add more carbon black to the flask after shaking if the filtrate is not clear. Filter through Whatman No. 40 or other suitable paper. Transfer a 5 ml aliquot of the filtrate to a 25 ml volumetric flask. If a smaller aliquot of filtrate is taken, make up the difference with sodium bicarbonate extractant solution. Slowly add 5 ml of ammonium molybdate hydrochloric acid solution and very cautiously shake the flask until the evolution of carbon dioxide subsides. Wash down the neck of the flask with distilled water and dilute to about a 20 ml volume. Add 1 ml of dilute stannous chloride solution, mix immediately by swirling, dilute to volume and mix. Read photometrically at 675  $\mu$  between 4 and 20 min after color development. The calibration standards should be prepared in the same manner including the 5 ml portion of extractant solution.

**Calculation**—

$$\frac{\text{Phosphorus in aliquot, micrograms} \times \text{extractant volume, milliliters}}{\text{aliquot, milliliters} \times \text{weight of sample, grams}}$$

= bicarbonate extractable phosphorus parts per million

#### AVAILABLE BORON<sup>114</sup>

With the exception of boron chemical methods of measuring the availability of elements required by plants in trace amounts are not well established.<sup>115</sup> Boron is a trace constituent of most soils although excessive amounts are sometimes encountered in soils of the arid regions giving rise to symptoms of boron toxicity in plants.<sup>116</sup> The determination of water soluble boron has been widely used as a measure of boron availability.

**Procedure**—Place 20 g of 2 mm soil in a 125 ml Florence flask of boron free glass. Add 40 ml of distilled water, attach a reflux condenser and boil for 5 min. Filter the suspension with suction on a Buchner funnel or centrifuge until the supernatant liquid is clear.<sup>117</sup> Place 20 ml of the clear extract in a platinum dish and add 5 drops of potassium carbonate solution<sup>118</sup> or place in a porcelain crucible and add 2 ml of a saturated solution of calcium hydroxide. Evaporate to dryness and ignite gently to destroy nitrates and all organic matter. Cool, add 5 ml of approximately 0.36 N sulfuric acid and triturate thoroughly with a policeman. Filter through a 9 cm paper and determine boron on a 1 ml aliquot of the filtrate as directed in the procedure for total boron. Boron above p. 2323.

**Calculation**—

$$\frac{\text{Boron in aliquot, micrograms} \times 10}{\text{weight of sample, grams}} = \text{available boron, parts per million}$$

<sup>113</sup> The carbon black should be pretreated to remove traces of phosphorus. Leach with sodium bicarbonate extractant solution, wash with water, and dry.

<sup>114</sup> *Tuog Soil Sci.* 59, 85-90, 1945. See also *Methods of Analysis* 38.

<sup>115</sup> See *Soil Chemical Analysis* 388-415 for a review of methods of determining availability of trace nutrients.

<sup>116</sup> See *Diagnosis and Improvement of Saline and Alkali Soils* 19 and 63.

<sup>117</sup> Add not more than 0.05 g of calcium chloride to aid clarification.

<sup>118</sup> Dissolve 40 g of anhydrous potassium carbonate in 100 ml of distilled water.

SOIL TESTING <sup>119</sup>

One task of the agricultural adviser is to make recommendations regarding the application of fertilizers and various amendments to the soil for the production of different crops. These recommendations are in effect predictions that are often based in part on data obtained from the analysis of the soil on which a particular crop is to be grown. The number of samples that must be processed is frequently very great, and systems of soil testing have been developed to facilitate rapid handling and analysis. The precision attained by routine soil test procedures is not ordinarily as great as that of standard quantitative methods of determining nutrient ion status, but their use is justified as a relatively economical way of obtaining information adequate for many agricultural purposes. The different types of solutions that have been used to extract nutrient ions vary greatly in pH value, ionic strength, buffer capacity, and qualitative composition. Some extractants are used for the removal of only 1 or 2 specific ions, others for measuring virtually all the common nutrient ions. Methods of analyzing the extracts include spectrophotometric, flame photometric, and spot-plate techniques. The various systems of nutrient extraction and determination do not differ in general principles from those on which standard quantitative methods (such as those given in the preceding portions of this section) are based. Although it is possible to rationalize a preference for a particular test procedure in some circumstances, it is often found that correlation between test results and crop response in the field is as good with one system of soil testing as with another. Other estimates of diagnostic value obtained in routine soil testing include pH value, lime requirement, organic matter content, and clay content. When one gains experience in working with soils of a given region, it is usually possible to make rough estimates of organic content and clay content by visual observation and tactile examination, respectively. Methods of soil testing will not be given here because of the lack of standardization at the present time.

<sup>119</sup> For reviews of chemical and biological test methods, see *Diagnostic Techniques for Soils and Crops*, and *Soil Chemical Analysis*, 339-69.

## Chapter 47

# VITAMINS

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**Introduction**—Historically, the dietary requirements of man and animal were considered to be fats, proteins, and carbohydrates as well as various inorganic salts. As technology advanced, it became apparent that there were other factors involved in nutrition. Several dietary deficiencies were observed under experimental conditions by workers such as Lunin (1881), Takaki (1885), Hopkins (1906), McCollum, Davis, Osborne, Mendel, and Eijkman. Funk, in a series of papers (1911, 1912), demonstrated that a substance was present in rice polishings that could be concentrated, purified, and used to cure paralysis in birds. He considered that this might be the missing factor involved in the human disease beriberi. Funk proposed the name *Vitamine* for this material since it appeared to be an amine and was vital for life. He is also considered to be the originator of the *vitamin hypothesis*, which states that certain diseases result from the absence of an indispensable dietary factor and that the resulting disease condition is called *avitaminosis*.

The term *Vitamine* did not of course apply to many newly discovered non-amine dietary factors, but the name was essentially retained although changed to *Vitamin* by subsequent workers in the field of nutrition. The vitamins were designated as either A or B, both of which are alcohol extractable, but the A group is fat soluble and the B group is water soluble. These traditional names have led to an awkwardness of nomenclature resulting in names such as vitamin B<sub>1</sub>, B<sub>2</sub>, B<sub>6</sub>, B<sub>12</sub>, etc. The A group has had to be divided into A, D, E, and K. In addition, other vitamins such as C, H, or biotin, inositol, and so on, were discovered that did not fit into either the A or B category. Many of the above vitamins have been relieved of their alphabetical listings and are now designated by names related to their structure.

The modern concept of a vitamin is that it is one of a group of organic compounds that are required for normal growth and maintenance of the lives of animals, including man. It further denotes a substance that is needed in amounts so small as to be of no significant value as a direct source of energy, as well as a material that is usually preformed in the diet of these animals. It is known that in the absence or serious deficiency of these compounds, clinical deficiency symptoms or abnormalities occur.

There are many known vitamins; many of these compounds that are considered vitamins for one species of animals are not considered as such for other species. This situation may exist because the animal does not require this compound or it can synthesize it in its own body, or the compound is produced by the bacterial



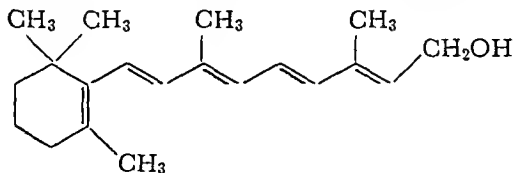
flora in the intestine of the animal. Even though most of the vitamins have been elucidated structurally, their rôle in the body is not yet completely clear. Many of them are known to be components of enzyme systems, and probably the main function of vitamins centers around their rôle in biological transformations.

The vitamins presented here are the ones normally encountered in the analysis of pharmaceutical formulations or clinical service work, and the authors do not pretend to cover all the vitamins known. The methods presented are a compilation covering the most used methods, provided they are satisfactory for routine use. In cases where conventional methods leave much to be desired, new methods, if available, have either been included or adequate references have been made, provided the authors believe that the new methods have definite advantages. Standard methods have, in many cases, been modified according to the experience of the authors or other workers<sup>1</sup> in these laboratories, in an effort to present, in the opinion of the authors, the most workable, precise, and accurate methodology available.

Of necessity, the mass of knowledge available from the many thousands of publications dealing with the analysis of vitamins has had to be condensed into a relatively few detailed methods. Where it was considered that other methods may be required for special problems, brief descriptions and references for some of these methods have been included.

### VITAMIN A

Vitamin A<sub>1</sub>, All-*trans* Vitamin A, Axerophthol

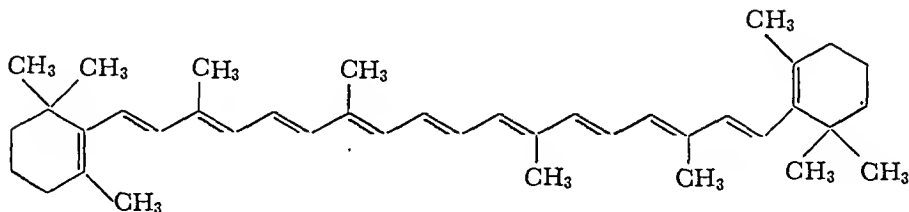


$C_{20}H_{30}O$

mol. wt. 286.44

Vitamin A is a derivative of carotenoid pigments, which are found widely distributed in the plant world. Especially rich in carotenes are carrots (0.01%), apricots, lettuce, cabbage, and spinach.

Karrer's<sup>2</sup> long and successful studies of carotenoid chemistry succeeded in total synthesis of several carotenoids such as



*Beta Carotene*

<sup>1</sup> The authors are indebted to Mr. Maurice E. Clark and his staff for many of the modifications of the methods included in this presentation.

<sup>2</sup> Karrer, P., Compt. Rend., 250, 1920, 1950.

In the body *beta* carotene breaks down to 2 molecules of vitamin A while *alpha* and *gamma* carotenes break down to form only 1 molecule of vitamin A. Rich sources of vitamin A are fish liver oils, butterfat, egg yolk, cheese, and liver.

Pure vitamin A acetate, dried in vacuum at low temperatures, occurs in the form of pale yellow prisms with *m p* 57° to 60°C. It exhibits no optical rotation. Vitamin A is soluble in most organic solvents and in oils; it is insoluble in water but can be easily dissolved as an aqueous phase by use of surface active agents. If exposed to ultraviolet irradiation it exhibits strong yellow fluorescence but undergoes destruction. Vitamin A is very sensitive to oxidation, the end product of oxidation being geronic acid. In acid media vitamin A is quite unstable but it appears to be fairly stable in alcoholic potassium hydroxide. The esters of vitamin A are more stable than the alcohol form.

Vitamin A exists in several geometric forms other than the all *trans* form. Of the other forms 2 *cis* vitamin A or Neovitamin A appears to be of most importance. These isomers have varying biological potencies and respond differently to the spectrophotometric assay. The Carr-Price Blue Color assay produces the same amount of color regardless of configuration.<sup>3</sup> It now appears that isomerization of all *trans* vitamin A may be a commercial problem and methods are being devised to measure the relative amounts of the various isomers; it is however beyond the scope of this text to describe these tests in detail. Suffice it to say that isomers with the 2 *cis* position such as 2 *cis*, 2,4 *di cis* and 2,6 *di cis* react slowly with maleic anhydride while all *trans* vitamin A reacts rapidly. This property is now being used to measure the relative amounts of these isomers in vitamin A products.<sup>4</sup>

## ULTRAVIOLET SPECTROPHOTOMETRIC DETERMINATION

Recently the spectrophotometric method was adopted as an international method.

**NOTE**—In 1954 the Food Division of the Applied Chemistry Section of the International Union of Pure and Applied Chemistry set up a Vitamin Assay Commission to study the spectrophotometric method. E. Brunius (J. AOAC 42, 657, 1959) reported on the results of this collaboration. The conclusion reached was that the spectrophotometric method should be used as a standardized method for vitamin A in the assay of oils in international trade. It set up 2 categories of oils: the first including most fish liver oils and vitamin A concentrates should measure the potency of the unsaponifiable matter isolated as described by the USP with correction by the Morton-Stubbs principle. The second category including whale liver oils and other oils having a high proportion of irrelevant absorption should require the chromatography of the unsaponifiable material before spectrophotometric measurement. The chromatographic method is described in the publication 1830 was recommended as a factor for the conversion of  $E_{1\text{cm}}^{1\%}$  at 325  $m\mu$  in isopropanol to all *trans* vitamin A units.

This method resulted from an evaluation of a great deal of work originally on the part of Coward<sup>5</sup> and has evolved as a result of the efforts of many other workers in various laboratories. Vitamin A has a maximum light absorption at about 325  $m\mu$  with a  $E_{1\text{cm}}^{1\%}$  of 1535 in isopropanol for the acetate and 1835 for the alcohol.<sup>6</sup> Experience with this method has revealed that quite often extraneous absorption was present concurrently with the vitamin A, resulting in misleading and invalid

<sup>3</sup> Ames S. J. Am. Chem. Soc. 77, 4134, 1955; J. AOAC 43, 21, 1960.

<sup>4</sup> Plack P. Biochem. J. 64, 56, 1956.

<sup>5</sup> Coward K. *et al.* Biochem. J. 25, 1102, 1931.

<sup>6</sup>  $E_{1\text{cm}}^{1\%}$  indicates the absorbancy of a solution containing 1 g. per 100 ml. contained in a cell having an absorption path of one centimeter (1 cm.).

high values. Morton and Stubbs<sup>7,8</sup> developed a correction for this absorption by measuring the light absorption at not only 325, but also at 310 and 334 m $\mu$  (wavelengths at which pure vitamin A has only 9% of its absorption at 325 m $\mu$ ). An equation has been devised for this correction, and has become a part of most official methods.

One of the problems with the spectrophotometric method has been the assessment of a value to convert  $E_{1\text{cm}}^{1\%}$  to biological potency. After several changes the present U.S.P. XVI value is 1830 for the conversion of  $E_{1\text{cm}}^{1\%}$  to all-*trans* vitamin A. *The British Pharmacopoeia, Addendum 1960*, uses the 1830 factor for vitamin A alcohol or saponified esters. For nonsaponified vitamin A esters, it uses 1900, measuring at 327.5 m $\mu$  in cyclohexane.

**Apparatus.** Spectrophotometer.—A suitable quartz spectrophotometer, which has been specially standardized for vitamin A, should be used. The cells should be either matched quartz or matched corex, 1-cm. cells. The difference in densities between the 2 cells, when both contain identically pure isopropanol, should be determined at 310, 325, and 334 m $\mu$ , and these differences, if any, should be applied to subsequent absorbance readings as positive or negative corrections. The instrument should be operated at the narrowest slit width consistent with good analytical technique. A given instrument should not be used if readings cannot be reproduced exactly on a given sample cell. The wavelength scale should be checked frequently against the 313.1 m $\mu$  and 334.1 m $\mu$  lines of a mercury lamp.

**Reagents.** Ethanol.—Use pure ethanol or redistilled ethanol.

Isopropanol.—Use redistilled isopropanol (99%). The following requirements for spectral purity must be met: the absorbance of the alcohol, with reference to distilled water in 1-cm. quartz cells, shall be no greater than 0.010 between 350 m $\mu$  and 320 m $\mu$ , and no greater than 0.050 at 300 m $\mu$ .

Sodium Sulfate.—Use sodium sulfate anhydrous granular coarse. It must not absorb vitamin A under the conditions described under saponification.

Ether.—Use freshly redistilled ether, discarding the first and last 10% cuts, or anhydrous ether without redistillation, if free from peroxides.

**Procedure.** Saponification and Extraction Procedure.—Transfer an accurately measured sample expressed in grams, milliliters, or dosage units, equivalent to not less than 0.15 mg. estimated vitamin A potency but containing not more than 1 g. of fat, to a boiling-separating flask<sup>9</sup> or a round bottom, saponification flask. Add 30 ml. of ethanol and 3 ml. of 50% aqueous potassium hydroxide solution. Place the flask under an all-glass reflux condenser, and reflux the mixture gently for 30 min. Add 30 ml. of distilled water while the flask is still hot, and swirl the contents until the mixture is homogeneous.

Quantitatively transfer the contents of the flask to a 250-ml., nonactinic, separatory funnel, rinse the flask with 30 ml. of ether, and transfer the ether to the separatory funnel (NOTE). (If a boiling-separating flask is used, no transfer is needed; the ether is added directly to the flask, and the first extraction and all washings are performed in the saponification flask.) Swirl, do not shake the first ether extraction, and then allow the layers to separate. Drain the lower aqueous

<sup>7</sup> Morton, R., Stubbs, A., *Biochem. J.*, 42, 195, 1948.

<sup>8</sup> Rogers, A., *Analyst*, 80, 903, 1955.

<sup>9</sup> The boiling-separating flasks have been used very successfully in the laboratories of the authors for many years, and are highly recommended for their ease of use, freedom from unnecessary transfers, and their protection of most of the vitamin A from light during the entire extraction process. See Brown, J. A., *J. Am. Pharm. Assoc.*, 40, 309, 1951.

## COLORIMETRIC METHODS

## CARR-PRICE METHOD

Various colorimetric methods of vitamin A determination have been proposed since Rosenheim<sup>13</sup> discovered that the purple color developed when some oils are treated with concentrated sulfuric acid was due to the presence of vitamin A. Fearon<sup>14</sup> proposed the use of trichloroacetic acid. Rosenheim<sup>15</sup> proposed a blue color developed with arsenic trichloride. The use of 1,3-dichloro-2-propanol was published by Sobel.<sup>16</sup> The Carr-Price<sup>17</sup> reaction with antimony trichloride, in spite of some difficulties, is still the most used color method. Brüggemann<sup>18</sup> proved that antimony pentachloride present in small quantities in antimony trichloride was responsible for the Carr-Price reaction.

**Apparatus.** Spectrophotometer.—Photoelectric colorimeter or spectrophotometer.

**Rapid Delivery, 10-ml. Automatic Pipet.**—Maximum delivery time, 2 sec.

**Reagents.** Antimony Trichloride Solution.—Corrosive reagent. Dissolve 100 g. of antimony trichloride in 400 ml. of chloroform by shaking and mild heating. Store overnight, and filter the solution through anhydrous sodium sulfate into an amber bottle.

**Reference Standard.**—Use U.S.P. vitamin A acetate reference solution in gelatin capsules containing 100,000 units per gram.

**Procedure.** Preparation of Calibration Curve.—Accurately weigh about 200 mg. of U.S.P. vitamin A acetate reference solution into a saponification flask, add a mixture of 30 ml. of ethanol and 3 ml. of a 50% aqueous potassium hydroxide solution. Proceed as in the spectrophotometric assay from "Place the flask under an all glass reflux condenser . . .," and continue through the remainder of the procedure.

Evaporate an aliquot of the ether to dryness under a stream of nitrogen or carbon dioxide. Dissolve the residue immediately in chloroform so that the final solution contains about 25 units of vitamin A per milliliter. Prepare a series of subsequent dilutions so that 4 different dilutions are available, containing about 5 to 25 units of vitamin A per milliliter.

To a spectrophotometric cell, transfer exactly 1 ml. of chloroform and 1 ml. of one of the standard dilutions prepared above. Place the cell in the instrument, add rapidly 10 ml. of the antimony trichloride reagent, and read the maximum color produced at 620 m $\mu$  against a blank of 2 ml. of chloroform and 10 ml. of reagent. Usually the maximum color occurs about 4 to 5 sec. after addition of the reagent. Determine the color response to each of the 4 concentrations of the standard, and plot the absorbances versus concentration to obtain a calibration curve. Frequent, if not daily, calibration curves are necessary; always prepare a new calibration whenever new antimony trichloride reagent is used.

**Analysis of the Sample.**—Accurately weigh or measure a sample estimated to contain 300 to 500 units of vitamin A, transfer to a saponification flask, and proceed as for the preparation of the calibration curve. Prepare a final chloroform

<sup>13</sup> Rosenheim, O., *et al.*, *Lancet*, 198, 862, 1920.

<sup>14</sup> Fearon, W., *Biochem. J.*, 19, 888, 1925.

<sup>15</sup> Rosenheim, O., *Biochem. J.*, 19, 753, 1925.

<sup>16</sup> Sobel, A., *et al.*, *J. Biol. Chem.*, 159, 681, 1945.

<sup>17</sup> Carr, F., Price, E., *Biochem. J.*, 20, 497, 1926.

<sup>18</sup> Brüggemann, J., *et al.*, *Fres. Z. Analyt. Chem.*, 135, 241, 1952.

solution to contain about 10 units of vitamin A per milliliter. Determine the color produced as above and from the calibration curve determine the potency of the final chloroform solution and then calculate the potency of the original sample by reference to the dilutions made during preparation of this chloroform solution.

**NOTE**—In certain samples the addition of the reagent to the sample may produce an opalescence. The addition of a few drops of acetic anhydride may correct this condition.

**NOTE**—If the sample is sufficiently concentrated (usually more than 20000 units per gram) it may not always be necessary to carry out the saponification and the sample may be diluted directly with chloroform and the color developed as above.

**NOTE**—Some laboratories<sup>19</sup> prefer to use more dilute antimony trichloride reagent thus slowing down color development and making the method somewhat easier to handle.

### PHOSPHOTUNGSTIC ACID METHOD

A new method has recently been developed by one of the authors<sup>20</sup> for determining vitamin A with phosphotungstic acid reagent (P T reagent) in ethyl acetate. The proposed method has wide applicability and appears to offer a convenient and rapid determination of vitamin A in a very large variety of vitamin A containing products.

One of the principal advantages of the P T reagent is the slow development of the blue color which reaches its maximum intensity 50 to 60 sec after the reagent has been added enabling the operator to easily determine maximum color for formation. The proposed method appears to have all the advantages of the antimony trichloride method and very few if any of the disadvantages. Because it is so new and has not been properly evaluated in enough laboratories it cannot as yet be recommended in an unqualified manner.

### VITAMIN A AND CAROTENES IN BLOOD

Most of the chemical methods for the determination of vitamin A in serum or plasma are based on the Carr-Price blue color method.<sup>21, 22, 23, 24</sup>

**Procedure**—In a 25 ml glass stoppered centrifuge tube pipet 5 ml of the serum or plasma and add an equal volume of 95% ethanol. After a short shaking interval add 12 ml of light petroleum ether and shake the contents for 10 min. The layers are separated by centrifuging.

A 10 ml aliquot of the clear supernatant petroleum ether solution is pipetted into a colorimetric cell and the optical density of the carotenes is read at 440 mμ against a petroleum ether blank. The amount of carotenes can be obtained by comparing the reading with a standard curve of pure beta carotene or a 0.0005% potassium dichromate solution which gives the same yellow color as a solution of beta carotene containing 1.12 μg per milliliter.

The petroleum ether is then evaporated under a stream of nitrogen or carbon dioxide at a temperature not exceeding 45°C. The residue is dissolved in 1 ml of chloroform and an exact amount of antimony trichloride reagent is added with 5 to 9 ml usually being used. The reagent should be added with a rapid

<sup>19</sup> Brown J. A. J. Am. Pharm. Assoc. 39: 699, 1950.

<sup>20</sup> Jakovljevic I. Pharm. Weekblad 95: 549, 1960.

<sup>21</sup> Kimble M. J. Lab. Clin. Med. 24: 1055, 1938.

<sup>22</sup> May Ch. et al. Am. J. Dis. Child. 59, June 1910.

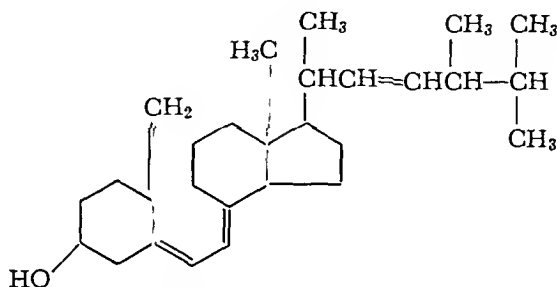
<sup>23</sup> McCoord et al. J. Nutrition 7, 557, 1934.

<sup>24</sup> Pett L., Le Page G. J. Biol. Chem. 132, 585, 1940.

delivery pipet. The optical density is read at 620  $m\mu$  against a blank of chloroform, and the amount of vitamin A calculated from a standard curve obtained from U.S.P. vitamin A reference standard solution treated as above. This reading should be corrected for the portion of the blue color due to the carotenes, which also react with antimony trichloride reagent. According to L. Pett and Le Page,<sup>24</sup> it was found that under their conditions 88.0  $\mu\text{g.}$  of *beta*-carotene give the same amount of blue color as 84.1 units of vitamin A.

The correction can be made also if carotenoid content in micrograms per 100 is multiplied by 0.4, and the product subtracted from total vitamin A content in units per 100 ml.<sup>25</sup>

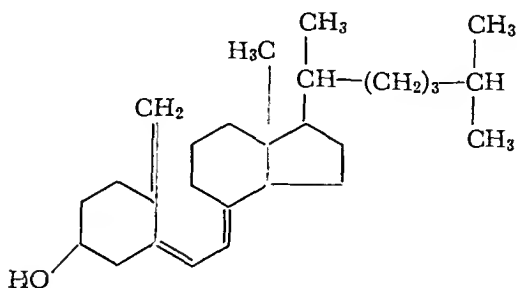
## VITAMIN D



Calciferol, Ergocalciferol

Vitamin D<sub>2</sub>C<sub>28</sub>H<sub>44</sub>O

mol. wt. 396.66



Activated 7-dehydrocholesterol

Vitamin D<sub>3</sub>C<sub>27</sub>H<sub>44</sub>O

mol. wt. 384.65

The existence of vitamin D as an antirachitic factor was found many years ago to be associated with vitamin A. Vitamin D activity was observed in irradiated oils and ergosterol. Windaus and Heilbron are credited with elucidating the structure of vitamin D<sub>2</sub>.

<sup>25</sup> Yudkin, S., *Biochem. J.*, 35, 551, 1935.

Vitamin D<sub>2</sub> is crystallized from acetone, and occurs in the form of white, odorless prisms, while vitamin D<sub>3</sub> is in the form of needles

<i>Vitamin D<sub>2</sub></i>	<i>Vitamin D<sub>3</sub></i>
m p 115° to 118°C	m p 84° to 86°C
[ $\alpha$ ] <sub>D</sub> = 103° to 106° (ethanol)	[ $\alpha$ ] <sub>D</sub> = 105° to 112° (ethanol)
[ $\alpha$ ] <sub>D</sub> = 52° (chloroform)	[ $\alpha$ ] <sub>D</sub> = 52° (chloroform)

Both vitamins are insoluble in water. They are soluble in ethanol, acetone, chloroform, ether, and oils. They are not precipitated by digitonin (different from ergosterol)

### QUALITATIVE TEST

To a solution of about 0.5 mg of vitamin D<sub>2</sub> or D<sub>3</sub> in 5 ml of chloroform add 0.3 ml of acetic anhydride and 0.1 ml of sulfuric acid and shake vigorously a bright red color which rapidly changes through violet and blue to green is produced (Liebermann reaction)

Pure vitamins D<sub>2</sub> and D<sub>3</sub> have a potency in humans of 40 USP units per microgram. Both vitamins are affected by light and air but under a neutral gas in brown bottles, and at low temperatures, they can be stored without decomposition for about 1 year.

Vitamin D in most cases especially in pharmaceutical formulations is in combination with vitamin A, and for many years that fact was a real challenge in the determination of vitamin D. Many attempts to solve the problems of interfering substances have been made such as the works of Brockmann and Chen<sup>26</sup> Sobel, *et al*<sup>27</sup> Tschapke, *et al*<sup>28</sup> DeWitt and Sullivan<sup>29</sup> and Stross *et al*<sup>30</sup>

The *British Pharmacopoeia*, 1958 (pp. 112-3), has included a method for pure material while the USP XVI has provided a method that is satisfactory for many multivitamin preparations. This method still is not suitable for certain samples such as irradiated yeast preparations, and care should be used in the application of the method. Recent experiences in these laboratories indicates that the method may not be entirely valid in the analysis of multivitamin preparations that have been purposely degraded at elevated temperatures. If there is any doubt about the validity of the chemical method, it should be checked by bioassay as a referee method. The described method is a modified USP XVI method.

### DETERMINATION OF VITAMIN D

**Apparatus.** Spectrophotometer.—Any suitable direct reading spectrophotometer. The instrument should be equipped with an attachment to hold a cell with a capacity of approximately 20 ml.

**Cells.**—Matched cells of about 20 ml capacity, and of test tube shape, such as Coleman's photofluorometer cuvetts 12190E, (19 by 105 mm) are used.

**Ultraviolet Lamp.**—This item should provide weak radiation in the 300 mμ region.

<sup>26</sup> Brockmann, H., and Chen, Y., *Z. Physiol. Chem.*, **241**, 129, 1956.

<sup>27</sup> Sobel, A., *et al*, *Ind. Eng. Chem., Anal. Ed.*, **17**, 160, 1945.

<sup>28</sup> Tschapke, H., *et al*, *Die Pharmazie*, **12**, 262, 1957.

<sup>29</sup> DeWitt, J., and Sullivan, *Ind. Eng. Chem., Anal. Ed.*, **18**, 117, 1946.

<sup>30</sup> Stross, P., Brealey, L., *J. Pharm. Pharmacol.*, **7**, 739, 1955.

**Reagents. Vitamin D Reference Solution. Stock Solution.**—Approximately 25 mg. of U.S.P. calciferol reference standard in 100 ml. of isooctane, accurately weighed to give a known concentration. Mix well and store in a refrigerator. At weekly intervals dilute 1 ml. of this solution with *n*-hexane to 25 ml., and determine the absorbance in 1-cm. cells at 265  $m\mu$  versus *n*-hexane blank. If the absorbance varies more than 5% from the original, discard the preparation.

**Reference Solution.**—One ml. of stock solution is evaporated to dryness in a stream of nitrogen gas; it is then dissolved in, and diluted to 50 ml. with, ethylene dichloride. This solution contains approximately 200 units of vitamin D per milliliter. This dilution must be used the day it is prepared.

**Potassium Hydroxide Solution.**—Dissolve 780 g. of potassium hydroxide in distilled water to make 1000 ml.

**Alcohol.**—Pure ethanol or redistilled ethanol.

**Florescens XXS.**—Chromatographic Fuller's earth.

**Chromatographic Siliceous Earth.**—(Celite No. 545, Johns-Manville Co. is satisfactory.) Boil a mixture of 150 g. of Celite No. 545 and 1 liter of 10% hydrochloric acid for 10 min. Cool, filter, and wash thoroughly with distilled water until the washings are neutral to methyl orange. Dry overnight at 100°C., and then ignite in a muffle furnace at 500°C. for 2 hr.

**Cottonseed Oil.**—Specific gravity of 0.915 to 0.921, solidification range of its fatty acids of 31° to 35°C., saponification value of 190 to 198, iodine value of 109 to 116; and the free fatty acids in 10 g. of the oil must require for neutralization not more than 2 ml. of 0.02 *N* sodium hydroxide. It must pass the test for trichloroethylene, in which 2 ml. of pyridine are added to 2 ml. of diluted sodium hydroxide (1 in 10) in a small test tube. Heat the mixture on a water bath at 90°C. for 5 min. Remove the tube, and add 1 ml. of the cottonseed oil without mixing the layers; no pink color forms in the pyridine layer within 20 min. It also must meet the following test for antioxidant properties:

Saponify 10 g. of the oil as directed in "Sample Preparation," under "Procedure," below, p. 2348, and dissolve the residue in 10 ml. of *n*-hexane. In a flask transfer 0.4 ml. of ferric chloride (1 in 1000) and 12 ml. of a (1 in 6000) solution of *alpha*, *alpha*'-dipyridyl in anhydrous ethanol, mix; and in 5 min. read the absorbance in a 1-cm. cell at 520  $m\mu$  versus anhydrous ethanol. Then add 0.2 ml. of the *n*-hexane solution of the residue above, and after 5 min. read the absorbance again at 520  $m\mu$ . The difference between the 2 readings must be not less than 0.125.

***n*-Hexane.**—Absorbance of this solvent is not more than 0.070 when measured in a 1-cm. cell at 300  $m\mu$ , with a suitable spectrophotometer against air as the blank.

**Isooctane (2,2,4-trimethylpentane).**

**Ethylene Dichloride (1,2-dichloroethane).**—This solvent may have to be redistilled and purified by passage through a column of granular silica gel.

**Antimony Trichloride Reagent. Solution A.**—Approximately 113 g. ( $\frac{1}{4}$ -lb. bottle) of antimony trichloride are emptied into 300 ml. of ethylene dichloride and dissolved. Add 2 g. of anhydrous alumina, filter into a reagent bottle, and dilute to 500 ml. with ethylene dichloride. Mix well. The absorbance of this solution in a 20-ml. cell described above must not exceed 0.070 when measured at 500  $m\mu$  versus ethylene dichloride.

**Solution B.**—Add 50 ml. of acetyl chloride to 200 ml. of ethylene dichloride, with mixing, and store in a glass-stoppered bottle.



**Color Reagent**—Pipet 10 ml of Solution B into a 100 ml volumetric flask and dilute to 100 ml with Solution A. Mix well. Do not use longer than 1 week or if any color develops.

**Color Inhibitor**—A solution containing equal volumes of acetic anhydride and ethylene dichloride. (A 25 ml volume is convenient.)

**Benzene**—Thiophene free

**PEG 600**—Polyethylene Glycol 600 Carbide and Carbon Chemical Company  
Carbowax

**Sodium Sulfate Anhydrous**—Granular coarse

**Phenolphthalein**—Dissolve 1 g of phenolphthalein in 100 ml of ethanol

**Sodium Sulfate Decahydrate**

**Columns** **Preparation of First Column**—To 25 g of prepared Celite No 515 add 100 ml of isooctane and then 10 ml of PEG 600 dropwise with stirring. The PEG 600 should contain as little water as possible. Transfer the slurry to a 2 cm by 25 cm glass column equipped with a coarse fritted disc and a stopcock sealed to a 0.5 cm by 5-cm exit tube. Pack each addition of slurry with vertical strokes of a plunger perforated by holes 2 mm in diameter. After all the slurry has been added pack the column by firm pressure of a solid disc on the settled Celite. The final column should be 15 to 16 cm in height. The column should not be allowed to run dry and a small amount of the mobile phase (isooctane) should always remain above the Celite. The packing of these columns is an art and consistently satisfactory columns can be packed after some experience has been obtained.

**Preparation of Second Column** Plug a tube (0.5 cm inside diameter by 25 cm length) with the bottom pulled out to a tapered constricted exit) with glass wool. Add to the tube enough Florex XXS so that the column is approximately 20 cm in length. Tap the side of the tube during and after the addition of the Florex to make the column sufficiently compact.

**Procedure** **Sample Preparation**—Transfer a sample equivalent to about 0.5 mg (or 10000 units)<sup>31</sup> of calciferol to a saponification flask. If no vitamin A is present add 3000 units of vitamin A acetate to provide the needed pilot bands in the subsequent chromatography. Add 2 ml of cottonseed oil then add 15 ml of potassium hydroxide solution and 50 ml of redistilled ethanol. Reflux for 30 min under an all glass reflux condenser. Cool and transfer the mixture to a 500 ml separator with the aid of 50 ml of distilled water rinsing the saponification flask. Add about 45 g of sodium sulfate decahydrate and 150 ml of *n*-hexane. Shake vigorously for 2 min. When the aqueous layer has separated transfer it to a second separator. Extract it with two 50 ml portions of *n*-hexane combine the hexane extracts and discard the aqueous solution.

Add to the combined hexane extracts about 50 ml of distilled water gently swirling the contents as the water is added. Allow to separate then drain and discard the water layer if it is clear. Do not drain off any emulsions or cloudy layers. Repeat the washings until the aqueous layer gives no pink color when tested with phenolphthalein solution.

Place a 2 cm layer of granular sodium sulfate anhydrous in a 30 ml coarse

<sup>31</sup> A larger sample can be used if desired and the washed hexane extract may be diluted to a larger volume than the 10 ml or if the potency of the sample is high enough evaporation of the *n*-hexane extract may not be necessary and the extract may be diluted to volume directly so that the concentration of the final extract is about 200 units per milliliter.

fritted glass funnel, and wash with *n*-hexane. Filter the washed *n*-hexane extracts through the sodium sulfate into a suitable Griffin beaker. Wash the flask and funnel with *n*-hexane to assure a quantitative transfer. Evaporate the extract to about 25 ml. on a steam bath, transfer quantitatively to a small round bottom flask, and evaporate to dryness under a stream of nitrogen. Quantitatively transfer the residue with *n*-hexane to a 10-ml. volumetric flask, and dilute to volume with *n*-hexane.

Allow the meniscus of the isooctane above the Celite column to enter just the Celite. Add 2 ml. of the sample from the preceding paragraph to the column. Allow the sample to flow into the Celite, and as the meniscus reaches the column surface, add the first of three 2-ml. portions of *n*-hexane, adding each succeeding portion as the preceding portion disappears into the column. Continue adding *n*-hexane in portions of 5- to 10-ml. until 100 ml. or more have been added. If necessary, adjust the flow rate to between 3 and 6 ml. per min. by application of gentle pressure at the top of the chromatographic tube. Discard the first 20 ml. of effluent, and collect the remainder. Examine the column under ultraviolet light at intervals during the chromatography, and stop the flow when the front of the fluorescent band, representing vitamin A, is about 5 mm. from the bottom of the column. Transfer the eluate to a suitable evaporation flask, and remove the *n*-hexane completely under vacuum at a temperature not above 40°C., or with a stream of nitrogen at room temperature. Dissolve the residue in *n*-hexane, and transfer to a 10-ml. volumetric flask or other suitable container. Rinse the evaporation flask with small portions of *n*-hexane to assist in this quantitative transfer and dilute to the volume mark. Mix well.

NOTE.—This column can be reused in many cases. Elute the vitamin A off the column, and then pass another 150 ml. of *n*-hexane over the column. Examine the column to see if all fluorescent bands have been removed, if the column has not obviously been contaminated with other materials, and if the flow rate is satisfactory. If it appears to be reusable, put about 200 ml. of isooctane, saturated with PEG 600, over the column to recondition it. Such columns have been used over 100 times in these laboratories over a 6-month period. Reuse of this column has another advantage in that the elution rates and volumes on the column remain relatively constant during repeated use, and allow the operator to standardize the column. If the ratio of A to D in the sample is greater than 10 to 1, a longer column may be necessary.

Place a 100-ml. beaker under the Florex column, and, with the aid of vacuum and a micro bell jar (or nitrogen pressure from above), add the sample from the preceding paragraph to the Florex column. Adjust the column flow to about 2 ml. per min. Rinse the volumetric flask with a total of 10 ml. of *n*-hexane in small portions, adding each portion to the column, allowing it to flow through the column and discard the effluent. When about 1 ml. of the *n*-hexane remains above the surface of the column, add 75 ml. of benzene, and elute with the aid of gentle suction (about 125 mm. of mercury), collecting the eluate. Evaporate the benzene under vacuum at a temperature not above 40°C., or with a stream of nitrogen at room temperature. Dissolve the residue in a small amount of ethylene dichloride, and transfer to a 10-ml. volumetric flask. Rinse the evaporation flask with ethylene dichloride and add to the 10-ml. volumetric flask to assure a quantitative transfer. Make to volume with ethylene dichloride, and mix well. This constitutes the sample solution and should contain approximately 200 units of vitamin D per milliliter.

**Color Reaction and Measurement of Absorption.**—All colorimetric measurements are made in matched 20-ml. tubes. Read the maximum absorbance, which occurs

about 30 to 45 sec. after addition of the color reagent, at 500  $m\mu$  with the instrument set at 0 absorbance versus ethylene dichloride. A second reading is made at 550  $m\mu$  90 sec. after the addition of the color reagent. The color reagent is added rapidly preferably from an automatic pipet.

The color reactions are carried out as follows: tube (a) 1 ml of sample solution + 1 ml of reference solution + 5 ml of color reagent; tube (b) 1 ml of sample solution + 1 ml of ethylene dichloride + 5 ml of color reagent; tube (c) 1 ml of sample solution + 1 ml of color inhibitor + 5 ml of color reagent.

Calculations —

$A$  = absorbance at 500  $m\mu$  of tube (a)

$B$  = absorbance at 500  $m\mu$  of tube (b),

$C$  = absorbance at 500  $m\mu$  of tube (c)

$D$  = absorbance at 550  $m\mu$  of tube (b)

$E$  = absorbance at 550  $m\mu$  of tube (c),

$F$  =  $\frac{\text{concentration of reference solution (in units per milliliter)}}{A - B}$ ,

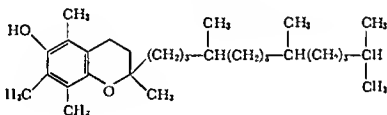
$G = [(B - C) - 0.67(D - E)]^{1/2}$  and

$F \times G \times \text{dilution factors} = \text{units of vitamin D per dimensions of sample}$

NOTE — The constant value of 0.67<sup>32</sup> is used to correct for vitamin A interference and is the ratio of the  $\Delta A_{500}$  to  $\Delta A_{550}$  value when only vitamin A is present. The  $\Delta A_{500}$  is  $B - C$  and  $\Delta A_{550}$  is  $D - E$ .

## VITAMIN E

*Alpha* Tocopherol Antisterility Vitamin



$C_{29}H_{50}O$

mol wt 430\*

The vitamin E group occurs mostly in plants especially in certain vegetables and seed germ oils. The best known of this group of vitamins are named *alpha*, *beta*, *gamma* and *delta* tocopherols and they differ in the number and location of the methyl groups. All of them are derivatives of *p*-hydroquinone and are thus good antioxidants. *Beta* and *gamma* tocopherols are about one half as active as *alpha* tocopherol and *delta* tocopherol has about one hundredth of the *alpha* tocopherol activity in the Evans resorption sterility test.

*Alpha* tocopherol is prepared synthetically as in the dl form (natural vitamin is d form) and occurs as a yellow clear viscous oil. It darkens in air and on exposure to light. It is insoluble in water, freely soluble in ethanol, acetone, chloroform, ether and in vegetable oils. *Alpha* tocopherol is very stable to heat and alkalies. It is easily oxidized by ferric ion. It boils at about 205°C. Density at 25°C. is 0.933 to 0.935.  $n_D^{25} = 1.5015$ . An ethanol solution of tocopherols gives an orange to

\* Wilke J. B. et al., J. Am. Pharm. Assoc., 47, 385, 1958.

red color by heating with nitric acid. Vitamin E produces a blue color if treated with vitamin K and cysteine.<sup>33</sup>

*Alpha* tocopherol is also found on the market in the form of the acetic acid ester, *alpha* tocopheryl acetate:  $C_{31}H_{52}O_3$ , mol. wt. 472.75. It is a pale yellow, viscous oil, which solidifies at  $-27.5^{\circ}\text{C}$ . It is insoluble in water, freely soluble in ethanol, chloroform, ether, and vegetable oils. In cyclohexane it has an absorption maximum at 285.5 m $\mu$ . Density at  $25^{\circ}\text{C}$ . is 0.955. *Alpha* tocopherol is also found as the succinate and is used as such in a number of pharmaceutical preparations.

Most chemical methods use the reducing properties of tocopherols, as in the method of reducing ferric chloride to ferrous salt, followed by a colorimetric procedure with  $\alpha, \alpha'$ -dipyridyl.<sup>34, 35, 36, 37</sup> Emmerie and Engel<sup>34</sup> were the first to use ferric chloride-dipyridyl reagent. Other methods use the decolorization of 2,6-dichlorophenol-indophenol by tocopherols,<sup>38</sup> or use nitric acid<sup>39</sup> as the reagent.

The interfering substances are usually carotenoids, vitamin A, cholesterol, and some unidentified substances. In the literature there are methods available for the separation of tocopherols.<sup>40</sup> The same authors use a new coupling reagent, 2,6-dichloro-*p*-benzoquinone-4-chlorimine.

The methods presented will be modified N.F. XI methods, which, in the opinion of the authors, will yield better, more reproducible results than the official methods.

## DETERMINATION OF THE TOCOPHEROLS

### ASSAY FOR ALPHA TOCOPHEROL

*Titrimetric Method.*—If *alpha* tocopherol is present in a relatively pure form, a simple titration with ceric sulfate may be made. Weigh accurately a sample equivalent to about 50 mg. of *alpha* tocopherol, transfer to an Erlenmeyer flask, and dissolve in 100 ml. of 0.5 *N* alcoholic sulfuric acid. Add 20 ml. of water followed by 2 drops of diphenylamine indicator (1 in 100 ml. of sulfuric acid), and titrate with 0.01 *N* ceric sulfate at the rate of about 2 to 3 drops per sec. The solution to be titrated should be stirred mechanically or swirled constantly during the titration until a blue end point is reached that lasts for about 10 sec. Run a blank on the reagents and make any corrections. Each milliliter of 0.01 *N* ceric sulfate is equivalent to 2.154 mg. of *alpha* tocopherol.

### ASSAY FOR ALPHA TOCOPHERYL ACETATE

*Titrimetric Method.*—Transfer about 250 mg. of *alpha* tocopheryl acetate, accurately weighed, into a 150-ml., nonactinic, round-bottom, standard-taper flask, and dissolve the sample in 25 ml. of dehydrated alcohol. Add 20 ml. of 5 *N* alcoholic sulfuric acid, connect the flask to an all glass reflux condenser, and reflux for 3 hr., while shielding the sample from light. Cool the mixture to room temperature, and transfer it quantitatively to a 200-ml., nonactinic, volumetric flask, and dilute to volume with dehydrated alcohol. Transfer exactly 50 ml. of the solution to a

<sup>33</sup> Cruz-Coke, E., *Nature*, 181, 49, 1958.

<sup>34</sup> Emmerie, A., *et al.*, *Rec. Trav. Chim.*, 57, 1351, 1938.

<sup>35</sup> Kaunitz, H., *et al.*, *J. Biol. Chem.*, 156, 653, 1944.

<sup>36</sup> Kaunitz, H., *et al.*, *J. Biol. Chem.*, 166, 205, 1946.

<sup>37</sup> Stern, M., *et al.*, *Anal. Chem.*, 19, 902, 1947.

<sup>38</sup> Scudi, J., *et al.*, *J. Biol. Chem.*, 146, 1, 1942.

<sup>39</sup> Furter, M., *et al.*, *Helv. Chim. Acta*, 22, 240, 1939.

<sup>40</sup> Green, J., *et al.*, *Analyst*, 84, 297, 1959.

250 ml Erlenmeyer flask, add 50 ml of 0.5 *N* alcoholic sulfuric acid, and proceed as in the method for *alpha* tocopherol from "Add 20 ml of water".

Each milliliter of 0.01 *N* ceric sulfate is equivalent to 2.364 mg of *alpha* tocopheryl acetate.

#### ASSAY FOR CONCENTRATES OF MIXED TOCOPHEROLS

These are natural concentrates that contain all the isomers of the tocopherols, and are usually assayed for total tocopherols and non *alpha* tocopherols, obtaining the amount of *alpha* by difference.

**Procedure Assay for Total Tocopherols**—Dissolve an accurately measured sample, equivalent to an estimated 15 mg of total tocopherols in sufficient dehydrated alcohol to make 100 ml. Mix well, and transfer a 2.0 ml aliquot of this solution to a nonactinic, 25 ml volumetric flask. Add 1 ml of a ferric chloride solution (1 in 500) in dehydrated alcohol, and time the reaction with a suitable timer. Immediately add 1 ml of  $\alpha,\alpha$  dipyridyl (1 in 200) in dehydrated alcohol solution, and mix thoroughly. Dilute to the mark with dehydrated alcohol and mix thoroughly. Determine the absorbance of the solution by means of a suitable spectrophotometer in 1 cm cells at 520  $m\mu$  versus a dehydrated alcohol reference, exactly 10 min after the addition of the ferric chloride solution. Perform a blank determination using the same quantities of the same reagents as above, except for the use of 2 ml of dehydrated alcohol instead of the sample solution. Subtract the reagent blank from the sample and multiply by 28.2 to calculate the milligrams of total tocopherols in the sample used. The 28.2 figure is obtained from average values obtained on mixtures of the *alpha*, *beta*, *gamma* and *delta* tocopherols usually present in such concentrates.

**Assay for Non *Alpha* Tocopherols**—Dissolve an accurately measured sample equivalent to an estimated 30 mg of non *alpha* tocopherol<sup>41</sup> in sufficient dehydrated alcohol to make exactly 100 ml. Mix and transfer a 5 ml aliquot of this solution to a nonactinic, 50 ml, glass stoppered cylinder. Add 0.2 ml of glacial acetic acid, and mix. Add 3.0 ml of a freshly prepared sodium nitrite solution (1 in 50) from a rapid delivery pipet, and shake the contents thoroughly for about 5 sec. After exactly 1 min, add 2 ml of a 20% potassium hydroxide solution, 10 ml of a 2% sodium sulfate solution, and exactly 12.0 ml of *n* hexane. Stopper the cylinder, shake the contents vigorously for 30 sec and allow the layers to separate. Transfer a portion of the upper layer to a 1 cm cell and measure the absorbance at 410  $m\mu$  versus an *n* hexane reference. Prepare a blank using the same reagents as above, except for the substitution of 5 ml of dehydrated alcohol for the sample. Correct the sample absorbance for the blank, and multiply by 40.8 to calculate the milligrams of non *alpha* tocopherols in the quantity of the sample used. The 40.8 factor is obtained from data on *beta*, *gamma*, and *delta* tocopherols usually present in mixed tocopherols concentrate. Calculate the amount of *alpha* tocopherol by difference based on this and the assay for total tocopherols above.

#### ASSAY FOR CONCENTRATES OF ALPHA TOCOPHERYL ACETATES

**Procedure. Sample Preparation**—Transfer an accurately measured quantity of *alpha* tocopheryl acetates, equivalent to an estimated 250 mg of total tocopheryl acetates, into a 250 ml, round bottom, standard taper, nonactinic flask. Add about 0.5 g of ascorbic acid and 50 ml of dehydrated alcohol. To the solution add 3 ml

<sup>41</sup> These concentrates usually contain about 35% total tocopherols, of which slightly less than 50% are non *alpha* tocopherols.

of 50% potassium hydroxide, connect to an all glass reflux condenser, reflux for 20 min., and cool to room temperature. Transfer the contents to a 500-ml., non-actinic, separatory funnel, and rinse the flask with about 100 ml. of water in several portions. Add 75 ml. of ether to the separator, and shake vigorously; allow the layers to separate, transfer the lower layer to another separator, extract it with 3 additional 25-ml. portions of ether, and add these ether extracts to the original extract. Wash the combined extracts by adding about 100 ml. of water and swirling the contents. Draw off the water layer and wash the ether extracts with additional water until the water washings no longer produce a pink color with phenolphthalein. Filter the washed ether extract through anhydrous sodium sulfate into a nonactinic, 250-ml. volumetric flask. Rinse the sodium sulfate filter with several portions of ether, then dilute to volume with ether, and mix thoroughly. Carry out the assay for both *alpha* and non *alpha* tocopheryl acetates in as short time as possible so that there will be no prolonged standing of the sample in ether solution.

**Assay for Total Tocopheryl Acetates.**—Transfer 15 ml. of the ether extract to a 100-ml., nonactinic volumetric flask, and evaporate the ether to dryness under a stream of nitrogen without the use of heat. After the ether has been evaporated, dilute the residue to 100 ml. with dehydrated alcohol, mix well, and proceed as under assay for total tocopherols in the method for concentrates of mixed tocopherols, starting with: “. . . and transfer a 2.0-ml. aliquot of this solution . . .”. Calculate the result by multiplying the absorbance of the sample corrected for blank by 32.0 to give the milligrams of total tocopheryl acetates in the 100 ml. of dehydrated alcohol solution; this value multiplied by 16.66 gives the number of milligrams of total tocopheryl acetates contained in the sample used. The 32.0 has been obtained from the most recent proportions of *alpha*, *beta*, *gamma*, and *delta* tocopherols in concentrates of *alpha* tocopheryl acetate. The 16.66 is a concentration factor indicating the portion of total sample represented in the 100-ml. alcohol solution.

**Assay for Non *Alpha* Tocopheryl Acetates.**—Transfer a 20-ml. aliquot of the ether extract of the unsaponifiable material above, to a 25-ml., nonactinic, volumetric flask, evaporate the ether to dryness in a stream of nitrogen, and then dilute to 25 ml. with dehydrated alcohol. Mix well. Proceed as in the assay for non *alpha* tocopherols under the method for concentrates of mixed tocopherols starting with: “. . . and transfer a 5-ml. aliquot of this solution . . .”.

Calculate the milligrams of non *alpha* tocopheryl acetates in the original sample used by multiplying the sample absorbance corrected for blank by 51.9, and then multiplying this by 3.125. The factor, 51.9, has been obtained from recent data on the *beta*, *gamma*, and *delta* tocopherol content in *alpha* tocopheryl acetate concentrate. The 3.125 is the equivalent of sample represented in 100 ml. of dehydrated alcohol solution, even though only 25 ml. were prepared for ease of assay. This conversion is necessary because the 51.9 factor has a concentration factor included, based on a 100-ml. volume. The *alpha* content is calculated by difference.

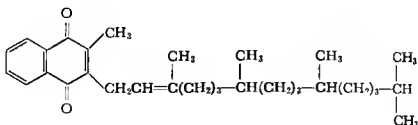
## VITAMIN K

The vitamin K group of vitamins is widely distributed in nature, especially in green plants (isolated from alfalfa by Dam and Karrer).<sup>42</sup> There are several vitamin K-like substances having the designations K<sub>1</sub>, K<sub>2</sub>, K<sub>3</sub>, etc.

<sup>42</sup> Dam, H., *et al.*, *Helv. Chim. Acta*, **22**, 310, 1939.

VITAMIN K<sub>1</sub>

Phytonadione, 2-Methyl-3-phytyl-1,4-naphthoquinone

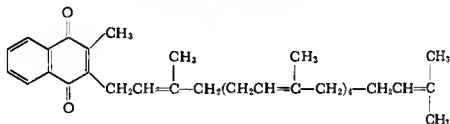
C<sub>21</sub>H<sub>46</sub>O<sub>2</sub>

mol wt 450.7

Vitamin K<sub>1</sub> is a clear, yellow, viscous liquid stable in air, but readily degraded on exposure to light. It is soluble in most organic solvents but insoluble in water. It is unstable in contact with reducing agents. Density at 25°C = 0.967.  $E_{1\text{cm}}^{1\%} = 428$  at 248 mμ. The refractive index at 25°C is between 1.5230 and 1.5250.

VITAMIN K<sub>2</sub>

2-Methyl-3-difarnesyl-1,4-naphthoquinone

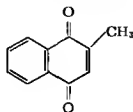
C<sub>41</sub>H<sub>56</sub>O<sub>2</sub>

mol wt 580.86

Vitamin K<sub>2</sub> occurs in the form of light yellow, micro crystalline plates. It is slightly less soluble than vitamin K<sub>1</sub> in the same solvents.  $E_{1\text{cm}}^{1\%} = 520$  at 249 mμ.

VITAMIN K<sub>3</sub>

Menadione, 2-Methyl-1,4-naphthoquinone

C<sub>11</sub>H<sub>8</sub>O<sub>2</sub>

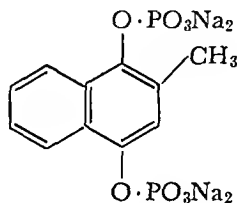
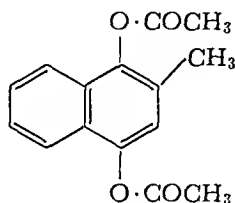
mol wt 172.2

Vitamin K<sub>3</sub> is a bright yellow, crystalline powder, stable in air, but unstable if exposed to sunlight. It is practically insoluble in water, but is soluble in benzene, ethanol, and vegetable oils. Melting point, 105° to 107°C. It is unstable in alkaline solutions, and is decomposed by reducing agents.

### VITAMIN K<sub>4</sub>

#### 2-Methyl-1,4-naphthoquinone hydroquinone

Usually found as the diacetate known as menadiol diacetate, or as the diphosphate known as menadiol diphosphate:



Tetrasodium diphosphate occurs as a white to pink powder. It is very soluble in water, insoluble in methanol, ethanol, and acetone, while the diacetate is almost insoluble in water, soluble in ethanol or acetic acid.

### DETERMINATION OF VITAMIN K<sub>1</sub>

**Spectrophotometric Method.**—Protect all solutions of this vitamin from exposure to light by use of nonactinic glassware. Transfer an accurately measured amount of sample, equivalent to about 100 mg. of vitamin K<sub>1</sub>, to a 100-ml. volumetric flask. Add 50 ml. of isopropanol, shake thoroughly to dissolve the sample, dilute to volume with isopropanol, and mix thoroughly. Let the mixture stand for 30 min., shaking occasionally; then allow any insolubles to settle to the bottom, or centrifuge a portion of the mixture if necessary. Dilute 1 ml. of the supernatant solution to 100 ml. with isopropanol. Determine the absorbance of this dilution at 270 mμ in a 1-cm. cell using a suitable direct reading spectrophotometer and isopropanol in the reference cell. Compare this absorbance to that of a 10 μg. per milliliter solution of U.S.P. phytonadione reference standard in isopropanol. This method is suitable for pure material or certain pharmaceutical formulations, except for emulsion of phytonadione, which requires a special modification as described in the U.S.P. XVI, p. 537.

### DETERMINATION OF VITAMIN K<sub>3</sub>

**Titrimetric Method.**—Accurately measure a sample, equivalent to about 20 mg. of menadione, and transfer to an Erlenmeyer flask. Extract the sample with 3 or more 10-ml. portions of chloroform, stirring the sample well each time, and after the insoluble material has settled, quantitatively transfer the supernatant extract to a medium porosity, sintered glass funnel protected from light. After the last extraction, transfer the entire sample to the funnel and rinse the flask and funnel with several small portions of chloroform. The funnel and suction flask should be protected from sunlight, and the suction flask should preferably be nonactinic. Evaporate the chloroform extracts to dryness using a current of air, but not with



the aid of a steam bath. Add to the residue 7 ml of glacial acetic acid, stir until dissolved and then add 10 ml of diluted hydrochloric acid (1 in 4) and about 1 g of zinc dust, and shake. Close the flask with a stopper having a pressure relief valve and allow to stand in the dark with occasional shaking for 1 hr. Quickly decant the solution through a pledget of cotton into another flask, and wash the original flask and cotton with three 5 ml. portions of boiled and cooled water. Add 0.1 ml of 1:10 phenanthroline (150 mg 1:10 phenanthroline in 10 ml of freshly prepared 148% ferrous sulfate) and titrate immediately with 0.02 *N* ceric sulfate. Run a blank titration and make any necessary correction. Each milliliter of 0.02 *N* ceric sulfate is equivalent to 1.722 mg of menadione.

If the sample being assayed contains stearic acid, the combined chloroform extracts should be extracted with 10 ml of 0.2 *N* sodium hydroxide, and the chloroform layer saved. The alkali layer is washed with 10 ml of chloroform and this chloroform is added to the main extract. The chloroform extract may have to be filtered and the filter washed with additional chloroform.

### POLAROGRAPHIC ASSAY

Very satisfactory results have been obtained in these laboratories using the method of Jongkind<sup>43</sup> as modified by Bourne<sup>44</sup>. This method can be used not only for the assay for pharmaceutical materials, but also to determine the amount of degradation of menadione for stability study purposes.

**Reagents.** Sorensen's Buffer pH 8—Add 6.75 g of potassium dihydrogen phosphate and 47 ml of 1 *N* sodium hydroxide to a 1000 ml volumetric flask. Dilute to volume with distilled water, and shake until dissolved.

Benzene, Reagent Grade.

Ethanol

**Standard**—Dissolve 50 mg of U.S.P. menadione reference standard in sufficient benzene to make 50 ml of solution. Store away from light.

**Ceric Solution**—Dissolve 13 g of ceric ammonium nitrate in sufficient 1 *N* sulfuric acid to make 500 ml of solution.

**Procedure for Menadione.**—Transfer an accurately weighed sample, equivalent to about 25 mg of menadione to a 125 ml, glass stoppered Erlenmeyer flask. Add exactly 25 ml of benzene, stopper, and shake on a wrist action shaker for 20 min. Filter through paper and transfer a 10 ml aliquot of the filtrate to a 50 ml beaker. Evaporate to dryness with the aid of an air stream. Dissolve the residue in 2 ml of ethanol, and quantitatively transfer to a 25 ml volumetric flask with the aid of several small portions of distilled water. Add 50 ml of Sorensen's buffer and dilute to the mark with distilled water. Adjust the mercury flow on a Sargent Polarograph Model XV (or any comparable polarograph), so that the drop rate is approximately 1 drop every 3 sec. Transfer approximately 15 ml of the sample solution to a rapid deaerating mercury pool type electrolysis vessel, and bubble nitrogen through the solution for three min. Keep the solution under an atmosphere of nitrogen while recording the curve. The polarogram is then recorded under the following conditions: 20 volt span, 0.030  $\mu$ a per millimeter sensitivity, damping in position 1, normal polarity, and over a span of 5 to 35%. Transfer a 2 ml. aliquot of the standard to a 50 ml beaker, and proceed as above, beginning 'Evaporate to dryness'. From the polarogram, obtain the wave heights for the standard and sample.

<sup>43</sup> Jongkind, J. C., Buzza, E., Fox, S. H., JAPHA, 46, 214, 1957.

<sup>44</sup> Bourne, R. J., private communication.

## Calculations.—

$$\frac{\text{Wave height of sample (millimeters)}}{\text{Wave height of standard (millimeters)}} \times 0.04 \times \frac{25}{10} \times \frac{25}{\text{sample weight (grams)}}$$

= milligrams of menadione per gram,

or:

$$\frac{\text{Wave height of sample (millimeters)}}{\text{Wave height of standard (millimeters)}} \times \frac{2.5}{\text{sample weight (grams)}}$$

= milligrams menadione per gram.

**Procedure for Menadiol and Menadione.**—Accurately weigh a sample equivalent to about 2.5 mg. of menadione into a 250-ml. iodine flask, and slowly add 25 ml. of ceric solution. Allow the foaming to subside, then add exactly 25 ml. of benzene. Stopper tightly and shake on a wrist action shaker for 20 min. Transfer the contents of the iodine flask to a 90-ml. centrifuge tube, and centrifuge for 5 min. Transfer a 10-ml. aliquot of the benzene layer to a 50-ml. beaker, and proceed as described under the procedure for menadione, beginning "Evaporate to dryness . . .". Transfer a 5-ml. aliquot of the standard to a 250-ml. iodine flask, add 25 ml. of ceric solution, exactly 20 ml. of benzene, and proceed as above.

## Calculations.—

$$\frac{\text{Wave height of sample (millimeters)}}{\text{Wave height of standard (millimeters)}} \times 0.04 \times \frac{25}{10} \times \frac{25}{\text{sample weight (grams)}}$$

= milligrams of menadione + menadiol per gram (calculated as menadione).

**NOTE.**—The N.F. XI, on p. 201, describes a 2,4-di-nitrophenylhydrazine method for menadione that works quite well for pure materials.

DETERMINATION OF VITAMIN K<sub>4</sub> DIPHOSPHATE

## TITRIMETRIC METHOD

**Procedure.**—Transfer an accurately measured sample, equivalent to about 50 mg. of vitamin K<sub>4</sub> diphosphate, to a 250-ml. beaker, and add 25 ml. of glacial acetic acid. Add 25 ml. of hydrochloric acid (1 in 4) and 25 ml. of water, mix, and titrate with 0.01 N ceric sulfate, using a potentiometric end point and a platinum-calomel electrode system. Each milliliter of 0.01 N ceric sulfate is equivalent to 2.651 mg. of menadiol sodium diphosphate hexahydrate, or 2.110 mg. of menadiol sodium diphosphate.

## SPECTROPHOTOMETRIC METHOD

**Procedure.**—Transfer a sample, accurately measured, equivalent to 10 to 100 mg. of menadiol diphosphate, to a 100-ml. volumetric flask. If the sample is not already in solution, dissolve it by adding a few drops of glacial acetic acid. Dilute to 100 ml. with water. Make further dilutions until the final concentration will be about 25 µg. per milliliter in Sorensen's buffer.<sup>45</sup> Determine the absorbance of this solution at 300 mµ using 1-cm. cells and any suitable direct reading spectrophotometer.

<sup>45</sup> Sorensen's buffer, pH 8. Add 6.75 g. of potassium dihydrogen phosphate and 47 ml. of 1 N sodium hydroxide solution to a 1000-ml. volumetric flask, and dilute to the mark with distilled water.

Use Sorensen's buffer in the reference cell. Compare this with the absorbance of a 20  $\mu$ g per milliliter reference standard in Sorensen's buffer.

### DETERMINATION OF VITAMIN K IN BIOLOGICAL MATERIALS

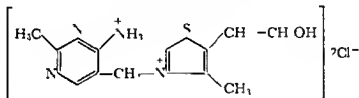
None of the above methods are suitable for use in biological materials. The method of Scudt and Buhs<sup>46</sup> has been used for biological materials but it is very lengthy and delicate. It involves a catalytic reduction of the quinone in butanol solution in the presence of phenosulfuric acid as an indicator. The resulting hydroquinone is treated with an excess of a butanol solution of 2,6-dichlorophenol indophenol. The decolorization is a measure of the vitamin K present in the sample.

The method of Kofler<sup>47</sup> has been used for urine and serum. It is based on the color reaction of 2-methyl-1,4-naphthoquinone with cyanoacetic acid ester and ammonia. A system of blanks is included to correct for interferences.

The most reliable method for biological materials still appears to be the bioassay.

### THIAMINE

Vitamin B<sub>1</sub> Aneurine



$C_{12}H_{17}ClN_4OS$

mol wt 337.79

Vitamin B<sub>1</sub> occurs in pharmaceutical preparations usually as the chloride hydrochloride or mononitrate. In nature vitamin B<sub>1</sub> is found either free or as a protein complex. Yeast and cereal grains are especially rich in vitamin B<sub>1</sub>.

Thiamine hydrochloride occurs as small white crystals or as a crystalline powder with a characteristic odor and bitter taste. It is very soluble in water. The pH of a 1% water solution is 3.1. It is soluble in glycerol and in ethanol but insoluble in acetone, benzene, chloroform, and ether. It melts between 246° and 250°C with decomposition. It does not show any optical rotation. Vitamin B<sub>1</sub> produces a white precipitate with mercuric chloride solution. In dry forms it is quite stable in air. On oxidation vitamin B<sub>1</sub> is converted into a yellow pigment called thiochrome which exhibits a strong blue fluorescence in ultraviolet light.

For quantitative measurement potassium ferricyanide in alkaline solution is used as an oxidizing agent<sup>48</sup> and this same method has been modified by many authors. To be able to determine not only free vitamin B<sub>1</sub> but also the ester form (pyrophosphoric ester) many authors have proposed an enzymatic hydrolysis.<sup>49, 50</sup>

<sup>46</sup> Scudt J V, Buhs R P, *J Biol Chem* 141, 451 1941 143, 665 1942

<sup>47</sup> Kofler M, *Helv Chim Acta* 28, 702 1945

<sup>48</sup> Jansen B, *Rec trav chim* 55, 1046 1936

<sup>49</sup> Hennessy D, *et al J Am Chem Soc* 61, 179 1939

<sup>50</sup> Melnick D, *et al J Biol Chem* 127, 531 1939

## DETERMINATION OF THIAMINE

## THIOCHROME ASSAY METHOD

**Apparatus.** Fluorophotometer.—Any suitable electronic fluorophotometer, such as the Coleman Model 12C, may be used for this determination. The primary filter should transmit energy at 365 m $\mu$ , and the secondary filter should be a narrow range transmittance filter with a transmission maximum at 435 m $\mu$ . Satisfactory filters are a Woods filter for primary, and Corning 3389 and 428 for a secondary filter. The energy source is a mercury vapor lamp.

**Cuvets.**—The fluorophotometer should be equipped with a matched set of cuvetts. These are available in sets of 12 for the Coleman instruments. If matched sets are not used, blank corrections must be determined for the difference in transmission of any 2 cuvetts used.

**Reagents.** Acid Potassium Chloride Solution.—Dissolve 250 g. of reagent potassium chloride in sufficient water to make approximately 950 ml. Add 8.5 ml. of reagent hydrochloric acid, and then sufficient water to make 1000 ml.

**Sulfuric Acid, 0.1 N.**—Add 3 ml. of reagent sulfuric acid to sufficient water to make 1000 ml.

**Sodium Hydroxide Solution, 15% w/v.**

**Digestion Mixture.**—Add 1 volume 0.1 N sulfuric acid to 1 volume acid potassium chloride.

**Potassium Ferricyanide Solution, 1%.**—Dissolve 0.5 g. reagent potassium ferricyanide in sufficient water to make 50 ml. This solution must be freshly prepared on the day it is used.

**Oxidizing Reagent.**—Prepare the solution by mixing 4.0 ml. of a 1% potassium ferricyanide solution with sufficient 15% sodium hydroxide solution to make 100 ml. *This solution must be freshly prepared on the day it is used.*

**Isobutyl Alcohol, Redistilled.**—Reagent grade isobutyl alcohol, redistilled in an all glass distillation apparatus.

**Sodium Acetate, 2 N.**—Dissolve 275 g. of reagent sodium acetate in sufficient water to make 1000 ml.

**Quinine Sulfate Stock Solution.**—Dissolve 10 mg. of quinine sulfate crystals in sufficient 0.1 N sulfuric acid to make 1000 ml. Preserve this solution in light-resistant containers in a refrigerator.

**Quinine Sulfate Standard Solution.**—Dilute 10 ml. of the quinine sulfate stock solution with sufficient 0.1 N sulfuric acid to make 400 ml. Preserve this solution in a refrigerator in light-resistant glassware, and add 2 to 3 ml. of redistilled chloroform to each 400 ml. of the solution. This solution fluoresces to approximately the same degree as the thiochrome obtained from 1  $\mu$ g. of thiamine hydrochloride, and is used to govern the reproducibility of the fluorophotometer. This solution should be carefully decanted into a cuvet in order that no chloroform will accompany the quinine solution and thus give a false fluorescent reading. A new quinine sulfate standard solution should be made up when there still remains approximately 100 ml. of the previous solution. After the new solution is standardized, the old solution can be discarded. A new solution must be made up at any time there is found to be a change of more than 2 galvanometer divisions deflection in the intensity of the fluorescence of the quinine solution from the intensity at the time the solution was first prepared.

**Thiamine Hydrochloride Stock Solution**—Weigh accurately 0.100 g of USP thiamine hydrochloride reference standard which has been kept in a desiccator over phosphorus pentoxide for at least 16 hr. Since the reference standard is hygroscopic precautions must be taken to avoid absorption of moisture during weighing. Transfer the weighed standard to a 1000 ml volumetric flask and dilute to volume with 20% ethanol which has been adjusted to a pH of 3.5 to 4.3 with hydrochloric acid. Store in the refrigerator in a well closed light resistant container.

**Thiamine Hydrochloride Standard Solution**—Pour 5 to 10 ml of the thiamine hydrochloride stock solution into a clean dry small glass stoppered flask. Store this solution in the dark and allow it to warm up to room temperature. Then by means of a clean dry pipet transfer 1 ml of the stock solution to a clean 100 ml volumetric flask and add sufficient water pH 3.5 to 4.3 to make 100 ml. Transfer exactly 5 ml of this solution to a clean dry 25 ml volumetric flask and add sufficient acid potassium chloride to make 25 ml. This is the standard solution and contains 0.20  $\mu\text{g}$  of thiamine hydrochloride per milliliter.

**Oxidation of Thiamine to Thiochrome and Measurement of Fluorescence**—Oxidation and Standardization—Take the 25 ml acid potassium chloride solution prepared as directed under thiamine hydrochloride standard solution above and transfer a 5 ml portion to each of two 30 ml glass stoppered separatory funnels. To each add 3 ml of the oxidizing reagent then 15 ml of isobutanol stopper and shake vigorously for a minimum of 90 sec. Centrifuge at slow speed to separate the alcohol and aqueous phases. Drain off the aqueous layer with a minimum loss of isobutanol. If the isobutanol layer is not water clear add about 2 g of anhydrous sodium sulfate. Decant the isobutanol from the separator into separate cuvetts in preparation for measurement of fluorescence.

Prepare a blank by treating 2 more 5 ml aliquots of the acid potassium chloride solution in exactly the same manner as directed in the paragraph above except that 3 ml of 15% sodium hydroxide are used instead of the 3 ml of oxidizing reagent. When the isobutanol solutions are ready to measure for extraneous fluorescence proceed as directed in the following paragraph.

Place in another matched cuvet 10 to 15 ml of the quinine sulfate standard solution. Now place in the fluorophotometer a cuvet containing the thiochrome from the standard thiamine solution (Oxidation and Standardization above) and adjust the instrument so that a reading of 50 divisions is obtained. Now measure the fluorescence of the blank solution as above. Replace the standard thiamine and readjust the instrument to read 50 divisions plus the reading obtained from the blank. Now place in the instrument the cuvet containing the quinine sulfate standard solution and determine the number of divisions deflection of the galvanometer produced by the fluorescence of the quinine. Check this reading with the duplicate thiamine and blank solutions just prepared. This quinine reading is equivalent to the fluorescence from 1  $\mu\text{g}$  of thiamine hydrochloride and the quinine solution standardized in this way may be used to standardize the fluorophotometer during subsequent measurements.

**Preparation of Assay Solution**—Transfer an accurately measured sample to a 250 ml nonactinic round bottom flask and add about 100 ml of digestion mixture. Reflux for 20 min cool and dilute to an estimated concentration of 1  $\mu\text{g}$  per milliliter. Transfer 5 ml of this dilution to a 25 ml volumetric flask and dilute to volume with acid potassium chloride. This is the assay solution.

**Oxidation of the Thiamine Hydrochloride from a Sample to Thiochrome and Measurement of the Fluorescence**—Take two 5 ml aliquots of the assay solution

prepared above, and oxidize as directed for the oxidation of the standard thiamine solution ("Oxidation and Standardization," above). Take another 5-ml. aliquot of the "assay solution" and prepare a blank as directed for the standard thiamine solution.

Measure the fluorescence of this oxidized assay solution and the blank against standardized quinine sulfate standard solution.

Calculations.—The microgram of thiamine hydrochloride represented in each milliliter of the final assay solution =

$$\frac{\text{fluorescence of sample solution} - \text{sample blank}}{50} \times 0.20$$

Calculate the quantity of thiamine hydrochloride in the assay sample on the basis of the dilutions used. Where necessary, the amount of thiamine mononitrate may be calculated by multiplying milligrams of thiamine hydrochloride by 0.9706.

#### METHOD FOR FOODS, CEREALS, OR LOW POTENCY SAMPLES CONTAINING THIAMINE

*Procedure.*—Weigh a sample estimated to contain 40 to 50  $\mu\text{g.}$  of thiamine, and transfer to a suitable digestion flask. Add about 150 ml. of 0.1 *N* hydrochloric acid, and mix well. Digest the mixture on a steam bath for about 30 min., shaking it occasionally. Cool the digested sample to room temperature and adjust the pH to 4.5 by adding 2 *N* sodium acetate, using a pH meter to check the pH, and dilute the sample to a definite volume.<sup>51</sup>

Transfer an aliquot of the digested sample, equivalent to about 5  $\mu\text{g.}$  thiamine, to a chromatographic tube of the Hennessy<sup>52</sup> type (about 125 to 150 mm. long, and 6-mm. diameter, fitted with an enlarged reservoir above and a capillary column at the bottom, allowing a flow rate of about 1 ml. per minute) filled with 1 to 2 g. of a purified base exchange silicate, such as Fisher Special Decalso for Thiochrome Determination.

After the sample has passed through the column, the column is washed with three 5-ml. portions of hot water, using care that the surface of the liquid never falls below the surface of the exchanger. Elute the thiamine by passing five 4.5-ml. portions of very hot acid potassium chloride through the column. Collect the eluate in a 25-ml. volumetric flask, cool the eluate, and dilute to volume with acid potassium chloride. This is the "assay solution"; proceed as in "Oxidation of the Thiamine Hydrochloride from a Sample to Thiochrome and Measurement of the Fluorescence," above. Calculate the results based on the size sample used and the dilutions made.

#### METHOD FOR THE DETERMINATION OF THIAMINE IN BLOOD

The procedure by T. Friedeman *et al.*<sup>53</sup> uses deproteinized blood, converting vitamin B<sub>1</sub> quantitatively to thiochrome, which is then determined fluorometrically. Because a portion of the vitamin B<sub>1</sub> in blood is in the form of its pyrophosphoric ester, it is necessary to apply an enzymatic hydrolysis to free the thiamine.

*Procedure.*—Five ml. of the blood are diluted to 30 ml. with water in a 100-ml.,

<sup>51</sup> An alternate enzyme hydrolysis may be performed as described in the AOAC, 9th ed., p. 658.

<sup>52</sup> Hennessy, D., *et al.*, J. Am. Chem. Soc., 61, 179, 1939.

<sup>53</sup> Friedeman, T., *et al.*, J. Lab. Clin. Med., 28, 1262, 1943.

glass stoppered centrifuge tube. One ml of about 1 N hydrochloric acid is added and well mixed by swirling and the mixture is heated for about 10 min in a boiling water bath. Takadiastase diastase or amylase (0.25 g) is added and the mixture is incubated for 1 to 1½ hr at 40°C. The mixture is then again acidified with 2 ml of 1 N hydrochloric acid heated in a boiling water bath for 10 min and then cooled to room temperature.

Ten ml of freshly prepared 10% metaphosphoric acid are then added and the volume is made up to 50 ml with water. The solution is mixed well and centrifuged.

An aliquot of 45 ml of clear supernatant liquid is transferred into a 150 ml Erlenmeyer flask. 2 drops of bromphenol blue indicator are added and by means of 1 N sodium hydroxide the pH is adjusted to 3 to 3.5.

The sample is then passed through a column of activated zeolite prepared in the following manner: <sup>54</sup> zeolite is activated by boiling several times with 5% acetic acid, washing with 25% potassium chloride and then with water until free of chloride; the zeolite is then packed into a 125 mm Hennessy column. After the sample has been passed through the column the column is washed with about 50 ml of water.

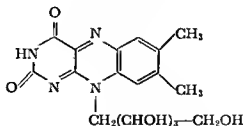
The thiamine is eluted with a 25% solution of potassium chloride or sodium chloride in 0.1 N hydrochloric acid until 25 ml of eluate is collected. This is the assay solution and is oxidized as in Oxidation of the Thiamine Hydrochloride from a Sample to Thiochrome and Measurement of the Fluorescence above.

#### DETERMINATION OF VITAMIN B<sub>1</sub> IN URINE

Many methods have been published for the determination of thiamine in urine but all appear to have rather serious shortcomings and will not be reviewed here. The methods of Perlzweig <sup>55</sup>, Mason and Williams <sup>56</sup> and Najjar and Ketron <sup>57</sup> are examples of various methods that have been used.

#### RIBOFLAVIN

Vitamin B<sub>2</sub> Lactoflavin Vitamin G



C<sub>17</sub>H<sub>20</sub>N<sub>4</sub>O<sub>6</sub>

mol wt 376.4

Riboflavin is widely distributed in both the plant and animal kingdom. It is a yellow or orange yellow crystalline powder with a slight odor and a somewhat bitter taste.

<sup>54</sup> This zeolite may be obtained as Special Decalco for Thiochrome Determination as supplied by Fisher Scientific Co.

<sup>55</sup> Perlzweig W *et al* Arch Biochem 6, 97 1945

<sup>56</sup> Mason H *et al* J Biol Chem 140 417 1941 146, 589 1942

<sup>57</sup> Najjar V *et al* J Biol Chem 152 579 1944

It is slightly soluble in water (about 0.01%), even less soluble in ethanol, and is insoluble in most other organic solvents. If 1 mg. is dissolved in 100 ml. of water, the solution is pale greenish-yellow, and has an intense yellowish-green fluorescence that disappears upon the addition of mineral acids or alkalies. It melts at about 280°C. with decomposition. Vitamin B<sub>2</sub> is optically active having a  $[\alpha]_D = -112^\circ$  to  $-122^\circ$  in a slightly alkaline water-ethanol solution. While it is stable in acids and some oxidizing agents (excluding chromic acid), it is easily reduced to a leuco base by sodium hydrosulfite. It is very sensitive to light. In natural products, it occurs in the form of esters; it is necessary, therefore, to hydrolyze samples before an analytical method is applied.

The fluorometric determination of vitamin B<sub>2</sub> is based upon activation by blue light at a wavelength of about 440 m $\mu$ . The fluorescence is very much affected by pH. Many methods have been proposed for the removal of interfering fluorescent substances. Some of the methods use activated earths, or treatment with permanganate and hydrogen peroxide, such as the method proposed by Koschara.<sup>58</sup> For products of low potency, some authors<sup>59</sup> have proposed a method that gives good agreement with microbiological assays. The preparation of samples for combined determination of riboflavin and thiamine is described by Conner.<sup>60</sup> For the determination of riboflavin in cereals, see the work of Andrews.<sup>61</sup>

## DETERMINATION OF VITAMIN B<sub>2</sub>

### FLUOROMETRIC ASSAY METHOD

**Apparatus.** Fluorophotometer.—Any suitable electronic fluorophotometer, such as a Coleman Model 12C, equipped with a primary filter transmitting at a maximum of 440 m $\mu$ , and a secondary filter with a maximum at 565 m $\mu$ . Representative filters are Corning Blue and Corning 038 as primary filters, and Corning 351 as a secondary filter.

**Cuvets.**—The fluorophotometer should be equipped with a matched set of cuvetts or cells. These are available in sets of 12 for the Coleman instrument. If matched sets are not used, blank corrections must be determined for the difference in transmission of any cuvetts used.

**Reagents.** Acetic Acid, Glacial, Reagent Grade.

Acetic Acid, 0.02 N.—Dilute 1.2 ml. of glacial acetic acid with sufficient water to make 1000 ml.

Acid Potassium Chloride Solution.—Dissolve 250 g. of reagent grade potassium chloride in sufficient water to make approximately 950 ml. Add 8.5 ml. of reagent hydrochloric acid and then sufficient water to make 1000 ml.

Sulfuric Acid, 0.1 N.—Add 3 ml. of reagent sulfuric acid to sufficient water to make 1000 ml.

Digestion Mixture.—Add 1 volume of 0.1 N sulfuric acid to 1 volume of acid potassium chloride.

Double-Normal Sodium Acetate.—Dissolve 275 g. of reagent sodium acetate in sufficient water to make 1000 ml.

Potassium Permanganate Solution.—Dissolve 4 g. of reagent grade potassium permanganate in sufficient water to make 100 ml.

<sup>58</sup> Koschara, W., *Bei.*, **67**, 761, 1934.

<sup>59</sup> Rubin, S., *et al.*, *Ind. Eng. Chem., Anal. Ed.*, **17**, 136, 1945.

<sup>60</sup> Conner, R., *et al.*, *Ind. Eng. Chem., Anal. Ed.*, **13**, 385, 1941.

<sup>61</sup> Andrews, J., *Cereal Chem.*, **21**, 398, 1944.



**Hydrogen Peroxide Solution.**—Use 3% solution

**Standard Riboflavin Stock Solution I.**—Dissolve 50 mg of U S P riboflavin reference standard previously dried at 105°C for 2 hr, and stored in the dark in a desiccator over phosphorus pentoxide, in 0.02 N acetic acid to make 500 ml. Store this solution under toluene in a refrigerator. Each milliliter represents 100 µg of U S P riboflavin reference standard. To facilitate solution add the 50 mg standard to approximately 300 ml of 0.02 N acetic acid, and warm the mixture on a steam bath with constant stirring until the riboflavin is dissolved. Then cool, and add 0.02 N acetic acid to make 500 ml.

**Standard Riboflavin Stock Solution II.**—To 100 ml of stock solution I, add 0.02 N acetic acid to make 1000 ml. Store under toluene in a refrigerator. Each milliliter represents 10 µg of U S P riboflavin reference standard.

**Standard Riboflavin Solution.**—Dilute 10 ml of stock solution II with water to make 100 ml. Each milliliter represents 10 µg of U S P riboflavin reference standard. Prepare fresh standard solution for each assay.

**Instrument Reference Solution.**—Dilute 1 ml of standard riboflavin stock solution II with water to make 100 ml. This solution is used to govern the reproducibility of the instrument each time the measurement of the fluorescence of test solutions (p. 2365 below) is to be made.

**Sodium Hydrosulfite.**—The sodium hydrosulfite must be of high purity. Do not use if unduly exposed to light or air. An amount appreciably in excess of 20 mg may reduce foreign pigmented and fluorescing substances, thereby causing erroneous results. The suitability of the sodium hydrosulfite is checked in the following manner: to each of 2 or more tubes add 10 ml of water and 1.0 ml of a standard riboflavin solution containing 20 µg of riboflavin in each milliliter and mix; to each tube add 1.0 ml of glacial acetic acid, mix; add, with mixing, 0.5 ml of potassium permanganate solution (1 in 25) and allow to stand for 2 min; then to each tube add, with mixing, 0.5 ml hydrogen peroxide solution, whereupon the permanganate color must be destroyed within 10 sec. Shake the tubes vigorously until excess oxygen is expelled. If gas bubbles remain on the sides of tubes after foaming has ceased, remove the bubbles by tipping the tubes so that the solution flows slowly from end to end. In the fluorometer, measure the fluorescence of the solution. Then add, with mixing, 8.0 mg of sodium hydrosulfite whereupon the riboflavin must be completely reduced in not more than 5 sec.

**Assay Procedure.** **Preparation of the Sample.**—Transfer an accurately measured amount of the sample to a 250 ml round bottom digestion flask, add 150 ml of digestion mixture, and reflux under an all-glass apparatus for 30 min or until the sample is disintegrated thoroughly. Transfer the contents to a 500 ml volumetric flask, dilute to volume with water, and mix. Filter the sample through a filter paper known to be free of fluorescent materials. Discard the first portion and dilute an aliquot of the subsequent filtrate so that a concentration of about 0.1 µg per milliliter is obtained. The final dilution is adjusted to a pH of 6.8 with 0.05 N sodium hydroxide before the final solution is diluted to volume. This constitutes the "assay solution."

**Preparation of Test Solutions.**—To each of 2 or more tubes, add 10 ml of the assay solution. To each of 1 or more of the tubes add 1.0 ml of the standard riboflavin solution and mix, and to each of 1 or more of the remaining tubes add 1.0 ml of water and mix. To each tube add 1.0 ml of glacial acetic acid, mix, and add, with mixing, 0.5 ml of potassium permanganate solution (1 in 25) and allow to stand for 2 min. Then to each tube add, with mixing, 0.5 ml of hydrogen peroxide solution, whereupon the permanganate color must be destroyed within

10 sec. Shake the tubes vigorously until excess oxygen is expelled. If gas bubbles remain on the sides of the tubes after foaming has ceased, remove the bubbles by tipping the tubes so that the solution flows slowly from end to end. Transfer the test solution from each tube to a clean dry cuvet.

**Measurement of Fluorescence.**—Place in the fluorophotometer a cuvet containing 10 to 15 ml. of the instrument reference solution, and adjust the instrument to give a deflection of 40 galvanometer divisions (or any other more desirable reading for any given instrument, providing the same setting is used from day to day). Measure the fluorescence of the test solution containing 1.0 ml. of added standard riboflavin solution, and call this reading *A*. Measure the fluorescence of the test solution containing 1.0 ml. of added water, and call this reading *B*. Then, to reduce the riboflavin present, add, with mixing, 20 mg. of sodium hydrosulfite to both of the tubes just read, and measure the fluorescence within 5 sec., and call this reading *C*. It is desirable that 3 or more galvanometer readings be made on each solution, and if minor variations occur, that the average readings be used.

**Calculations.**—

The micrograms of riboflavin in each milliliter of the "assay solution" =  $\frac{B - C}{A - B} \times 0.1$ .

The ratio of  $(B - C)/(A - B)$  must be not less than 0.66 or more than 1.5. The riboflavin content of the sample is calculated from the aliquots used for assay and the size of the original sample used.

**Alternative Sample Preparation.**—An alternative method of sample preparation is used for special cases such as foods, low potency natural products, etc., in which the sample is placed in a flask and an amount of either 0.1 *N* sulfuric or hydrochloric acid is added so that a concentration of less than 0.1 mg. of riboflavin per milliliter is obtained. Usually a 30- to 50-ml. portion of acid is used. The mixture is then heated in an autoclave at 121° to 123°C. for 30 min., and then the sample is cooled. If any clumping has occurred during autoclaving, mix thoroughly until the particles are evenly suspended. Adjust the pH of the solution to 6.0 to 6.5 with sodium hydroxide solution, and then add dilute hydrochloric acid until no further precipitation occurs.

Dilute the mixture to a definite volume so that a concentration greater than 0.1 µg. per milliliter is obtained, and mix thoroughly. Filter through a paper known not to contain fluorescent material. Centrifuging or the use of a filter aid may be employed for materials that are difficult to filter. To an aliquot of this filtrate, add more hydrochloric acid and then sodium hydroxide to check for complete precipitation of protein. If no further precipitate forms, adjust the solution to a pH of 6.8, and dilute to a volume so that a calculated concentration of 0.1 µg. per milliliter is obtained. Filter again if necessary. This is the "assay solution"; proceed as above.

### SPECTROPHOTOMETRIC METHOD

In pure solution riboflavin can be assayed by direct reading of its color at 444 mµ, as proposed in the *British Pharmacopoeia*.<sup>62</sup>

### RIBOFLAVIN IN URINE

The method is adapted from the work of V. Najjar.<sup>63</sup> The urine for riboflavin determination must be preserved with about 3% of glacial acetic acid, and kept in

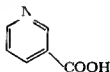
<sup>62</sup> British Pharmacopoeia, 1958, p. 509.

<sup>63</sup> Najjar, V. A., J. Biol. Chem., 141, 355, 1941.

dark bottles. If normal content of riboflavin is expected, 1–2 ml of urine are diluted to 5 ml with water, or if a deficiency is anticipated, a 5 ml sample of urine is used. In a 30-ml, glass stoppered centrifuge tube add 5 ml of diluted or undiluted urine, 1 ml of glacial acetic acid, and 1 ml of pyridine, and shake well. Then add 2 drops of 4% potassium permanganate for each milliliter of actual urine, and let stand for 2 min. The solution is then mixed for several seconds. The excess of potassium permanganate is then destroyed with 3% hydrogen peroxide. Add 1 g of anhydrous sodium sulfate for each milliliter of undiluted urine, and then 10 ml of *n*-butanol and shake well for 2 min. Centrifuge to separate the layers. Transfer an aliquot of the upper layer (butanol pyridine) to a photometric cell, and determine the fluorescence in a suitable fluorophotometer as above.

## NICOTINIC ACID

Niacin, Pyridine- $\beta$ -carboxylic Acid, Anti Pellagra Vitamin, P P Factor



$C_6H_5NO_2$

mol wt 123.11

Niacin is found in yeast, meat, fish, alfalfa, corn, legumes, and is a constituent of coenzymes I and II. In animal tissue it is found as the amide.

Niacin occurs in the form of a white crystalline powder, or in the form of needles (from water and ethanol). One g dissolves in about 60 ml of water and is soluble in solutions of alkali hydroxides and carbonates. It is insoluble in ether. The melting point is  $234^\circ$  to  $237^\circ C$  (sublimes without decomposition). If a small quantity is heated with soda lime, it develops the odor of pyridine.

## DETERMINATION OF NICOTINIC ACID

### TITRATION METHOD

For the pure material, dissolve about 250 mg in 50 ml of water, and titrate with 0.1 *N* sodium hydroxide, using phenolphthalein as the indicator. Each milliliter of 0.1 *N* sodium hydroxide is equivalent to 12.31 mg of nicotinic acid.

### CYANOGEN BROMIDE METHOD

Various methods have been proposed for the quantitative determination of nicotinic acid based on the reaction with cyanogen bromide to give an intermediate pyridinium compound, which in turn is decomposed and coupled with an aromatic amine to produce a color.<sup>64 65 66,67 68 69</sup>

<sup>64</sup> Dann W, *et al*, J Biol Chem, 136, 729, 1940

<sup>65</sup> Harris, L., *et al*, Biochem J 33, 2037, 1939

<sup>66</sup> James, E., *et al*, Analyst, 72, 327, 1947

<sup>67</sup> Melnick, D., Cereal Chem, 19, 553, 1912

<sup>68</sup> Melnick, D., *et al*, Ind Eng Chem, Anal Ed, 15, 355, 1943

<sup>69</sup> Perlezwieg W, *et al*, J Biol Chem, 136, 729, 1940

**Apparatus.** Spectrophotometer.—Any suitable direct reading spectrophotometer can be used.

**Reagents.** Cyanogen Bromide Reagent.—Dissolve cyanogen bromide in distilled water to make a 10% solution. *Prepare this solution under a hood*, as cyanogen bromide volatilizes at room temperature, and the vapor is extremely hazardous.

**Sulfanilic Acid Solution.**—To 10 g. of sulfanilic acid, add 60 ml. of water and 12 ml. of 10% ammonia. Mix, and add with stirring, more of the ammonia if necessary, until the acid dissolves; adjust the pH of the solution to about 4.5 with diluted hydrochloric acid, and dilute to 100 ml.

**Standard Preparation.**—Weigh accurately 75 mg. of U.S.P. nicotinic acid reference standard into a 50-ml. Erlenmeyer flask, and, after dissolving the standard in about 20 ml. of water, transfer it quantitatively to a 250-ml. volumetric flask, and make up to volume with water. Pipet 10 ml. of the solution into a 200-ml. volumetric flask, and make up to volume with water. This solution contains 15  $\mu$ g. of standard per milliliter.

**Sample Preparation.**—Prepare a water solution of the sample, using heat if necessary, to contain in each milliliter about 15  $\mu$ g. of nicotinic acid. This is the "assay solution."

**Procedure.**—Mark 4 test tubes 1, 2, 3, and 4. Pipet into each test tube the standard preparation, assay solution, ammonia dilution (1 ml. stronger ammonia diluted with water to 50 ml.), and water as indicated in the chart below (for details see the following paragraphs):

	<i>Tube 1</i> <i>ml.</i>	<i>Tube 2</i> <i>ml.</i>	<i>Tube 3</i> <i>ml.</i>	<i>Tube 4</i> <i>ml.</i>
Standard preparation	1.0	1.0	—	—
Assay solution	—	—	1.0	1.0
Ammonia dilution	0.5	0.5	0.5	0.5
Water	6.5	1.5	6.5	1.5

From this point on, all steps should be carried out under a hood, using careful analytical technique to avoid breathing the fumes from the cyanogen bromide. To Tube 1, add 2.0 ml. of the sulfanilic acid solution, shake well, and add 1 drop of hydrochloric acid. Mix the solution thoroughly, and place in the spectrophotometer. Adjust the instrument to zero absorbance at 450  $m\mu$ . To Tube 2, add 5.0 ml. of the cyanogen bromide reagent, mix, and exactly 30 sec. after completion of the addition of the cyanogen bromide, add 2.0 ml. of the sulfanilic acid solution with swirling. Measure the absorbance of the solution from Tube 2 at 450  $m\mu$  against the solution from Tube 1 as a blank, designating the reading as standard (read the maximum absorbance).

Perform the same procedures respectively for Tubes 3 and 4, designating the reading of the solution from Tube 4 as sample.

**Calculations.**—

$$\frac{\text{Absorbance of sample}}{\text{Absorbance of standard}} \times 15$$

$$= \text{micrograms of nicotinic acid per milliliter of "assay solution"}$$

The nicotinic acid content of the test material is calculated on the basis of the sample size, aliquots, and dilutions made during the assay.

## NICOTINIC ACID IN URINE

**Reagents** Cyanogen Bromide Reagent—Use the same reagent as described above

**Amine Reagent**—Five g of *p*-aminacetophenone is dissolved in 14 ml of 10% hydrochloric acid and diluted with water to 50 ml

**Procedure**—The method is based on the work of L. Harris<sup>6</sup> All work with cyanogen bromide should be carried out in a well ventilated hood To 20 ml of urine in a 100 ml round bottom flask add 5 ml of a 20% sodium hydroxide solution Fit the flask with a condenser and heat for 30 min on a steam bath to hydrolyze the amide

The mixture is cooled to room temperature and the pH is adjusted to exactly 6.0 using bromthymol blue as an external indicator The contents are then quantitatively transferred to a 50 ml glass stoppered graduate and made up to volume with water

Three 20 ml test tubes are marked at the 15 ml mark with an ampoule file and labeled B, C and S B is a blank and S is the sample C is the control tube to which is added 0.20 ml of a standard solution of nicotinic acid containing 100 µg per milliliter Ten ml of the hydrolyzed urine are pipetted into each test tube and then heated for 10 min in an 80°C bath located in a well ventilated hood

Two ml of the cyanogen bromide reagent are added to C and S tubes and heating is prolonged for another 4 min The tubes are placed in a cold water bath and after 4 min 0.2 ml of amine reagent is added to all tubes The tubes are placed in a dark place for 15 min To each tube 0.4 ml of 10% hydrochloric acid is added and made up to 15 ml with water The tubes are again placed into a dark place for 15 min The readings are taken in 2 or 3 cm cells at 470 mµ against a reference solution of water

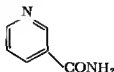
**Calculations**—

$$\frac{\text{absorbance (sample)} - \text{absorbance (blank)}}{\text{absorbance (control)} - \text{absorbance (sample)}} \times \frac{20}{\text{milliliters of urine}}$$

= micrograms of combined nicotinic acid, nicotinamide, and several metabolites of these all expressed as nicotinic acid

## NICOTINAMIDE

Niacinamide, Nicotinic Acid Amide Vitamin B<sub>3</sub> Vitamin PP



C<sub>6</sub>H<sub>6</sub>N<sub>2</sub>O

mol wt 122.13

As in the case of nicotinic acid nicotinamide occurs in both the plant and animal worlds usually associated with enzyme systems Niacinamide occurs in the form of a white crystalline powder or as needles (from benzene) It is very soluble in water and ethanol easily soluble in glycerol and slightly soluble in ether Niacinamide

melts between 128° and 131°C. It sublimes without decomposition. If heated with a solution of sodium hydroxide, the odor of ammonia is perceptible.

## DETERMINATION OF NICOTINAMIDE

### NONAQUEOUS TITRATION METHOD

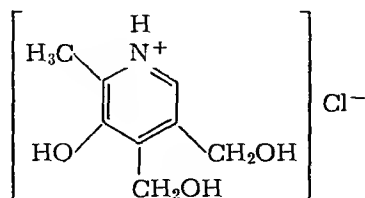
*Procedure.*—Dissolve 200 to 250 mg. of nicotinamide, accurately weighed, in 20 ml. of glacial acetic acid, and, if necessary, heat gently to effect solution. Add 100 ml. of benzene with a graduate, 2 drops of methylrosaniline chloride indicator (100 mg. of methylrosaniline chloride in 10 ml. of glacial acetic acid), and titrate with 0.1 *N* perchloric acid. Perform a blank determination omitting the nicotinamide, and make any necessary correction. Each milliliter of 0.1 *N* perchloric acid is equivalent to 12.21 mg. of nicotinamide.

### CYANOGEN BROMIDE METHOD

Prepare the cyanogen bromide solution, sulfanilic acid solution, standard preparation (using U.S.P. nicotinamide reference standard), and sample preparation as described for nicotinic acid. The procedure is the same as for the nicotinic acid.

## PYRIDOXINE

Vitamin B<sub>6</sub>, Adermine, Pyridoxine Chloride



$C_8H_{12}NO_3 \cdot Cl$

mol. wt. 205.64

In pharmaceutical preparations, vitamin B<sub>6</sub> is usually found as the hydrochloride. It is widely distributed in the plant and animal worlds, especially in yeast, liver, and cereals.

Vitamin B<sub>6</sub>, as the hydrochloride, is in the form of white or colorless crystals (platelets or rods), and is stable in air. One g. dissolves in 5 ml. of water and about 1% in ethanol. It is sparingly soluble in acetone, insoluble in ether; it is stable in acidified solutions.<sup>70</sup> It melts at about 205°C. with decomposition.

Many methods<sup>71, 72, 73, 74, 75</sup> have been developed for the analysis of pyridoxine, some of which have been modified many times, but the most used methods are those using indophenol, as well as those using 2,6-dichloroquinone-chlorimide.

<sup>70</sup> Cunningham, E., *et al.*, J. Biol. Chem., 158, 491, 1945.

<sup>71</sup> Bina, A., J. Biol. Chem., 148, 111, 1943.

<sup>72</sup> Hochberg, M., *et al.*, J. Biol. Chem., 155, 109, 119, 129, 1944.

<sup>73</sup> Scudi, J. V., *et al.*, Proc. Soc. Exp. Biol. Med., 43, 118, 1940.

<sup>74</sup> Stiller, E., *et al.*, J. Am. Chem. Soc., 61, 1237, 1939.

<sup>75</sup> Swaminathan, M., Nature, 145, 780, 1940.

## DETERMINATION OF PYRIDOXINE HYDROCHLORIDE

## NONAQUEOUS TITRATION METHOD

For the pure compound a simple nonaqueous titration is satisfactory if specificity is not desired. This titration can be done by weighing accurately about 400 mg of sample and transferring it to a 150 ml beaker. The sample is dissolved in a mixture of 40 ml of glacial acetic acid and 10 ml of 5% mercuric acetate in glacial acetic acid and heated slightly to effect solution. Cool the sample, add 2 to 3 drops of methylosaniline chloride (100 mg in 10 ml glacial acetic acid) and titrate with standardized 0.1 N perchloric acid. Run a blank by titrating the same amount of reagents as used in the sample and make any necessary corrections. Each milliliter of 0.1 N perchloric acid is equivalent to 20.56 mg of pyridoxine hydrochloride.

## SPECTROPHOTOMETRIC METHOD

Pure material may also be easily assayed by making up a 10  $\mu$ g per milliliter solution in 0.1 N hydrochloric acid and determining its absorbance at 292 m $\mu$  versus a blank of 0.1 N hydrochloric acid. This absorbance is compared to a standard of USP pyridoxine hydrochloride reference standard obtained in the same manner.

## COLORIMETRIC METHOD

Scudi and coworkers<sup>76, 77</sup> developed a method of analysis based on the reaction of pyridoxine with 2,6-dichloroquinone chlorimide. This method was later modified by Hochberg<sup>78</sup> and a modification of their method is described here. Elucidation of the structure of the B<sub>6</sub> group, including the presence of pyridoxal and pyridoxamine, has cast considerable doubt on the validity of this method for natural products. Both pyridoxal and pyridoxamine, as well as other physiologically active B<sub>6</sub> group members, react with this reagent to varying degrees; this method can therefore be recommended only for samples that contain the major portion of their B<sub>6</sub> activity as pyridoxine.

**Apparatus** Spectrophotometer—Any suitable direct reading spectrophotometer.

**Reagents** Chlorimide Reagent—Recrystallized 2,6-dichloroquinone chlorimide should be used and if unavailable the reagent may be recrystallized by dissolving 1 g in 50 ml of acetone and gradually adding about 200 ml of water with continuous stirring. The crystals are collected on a filter pad and air dried by suction. The dry reagent, when stored in a tightly sealed bottle in a refrigerator, is stable for at least 6 months. To prepare the reagent solution, 40 mg of the recrystallized reagent are dissolved in 100 ml of isopropanol. The solution must be kept in a glass stoppered bottle in a refrigerator and should not be kept for more than 1 month or should be discarded as soon as a pink coloration develops.

**Ammonia-Ammonium Chloride Buffer**—Dissolve 16 g of ammonium chloride in 70 ml of water, add 16 ml of stronger ammonia water (27%) and dilute to 100 ml with water, mix and filter.

**Sodium Acetate Buffer**—Dissolve 20 g of sodium acetate  $3H_2O$  in water and dilute to 100 ml with water.

**Boric Acid Solution**—Dissolve 5 g of boric acid in 90 ml of hot water, cool and dilute to 100 ml.

<sup>76</sup> Scudi, J. V. *et al.* *Proc. Soc. Exp. Biol. Med.* 136, 399, 1940.

<sup>77</sup> Scudi, J. V. *Proc. Soc. Exp. Biol. Med.* 139, 707, 1941.

**Standard Preparation.**—Accurately weigh exactly 25 mg. of U.S.P. pyridoxine hydrochloride reference standard, previously dried in vacuum over silica gel for 4 hr., transfer to a 250-ml., nonactinic volumetric flask, dilute to volume with 0.1 *N* hydrochloric acid, and mix thoroughly. If this solution is kept in a glass-stoppered flask in a refrigerator, it should be stable for at least 3 months. Prepare a dilution of this standard daily, making a 10 to 100 dilution in water.

**Assay Procedure.**—Transfer a finely ground sample, equivalent to about 10 mg. of pyridoxine hydrochloride, to an Erlenmeyer flask, and add 5 ml. of hydrochloric acid and about 250 ml. of water. Alternatively, the sample can be dispersed in a blender and then transferred to an Erlenmeyer flask. The sample is heated on a steam bath for about 15 min., or until the sample is thoroughly dispersed. The sample is cooled and transferred to a 500-ml. volumetric flask, diluted to volume, and mixed. A 25-ml. aliquot is transferred to a 50-ml. volumetric flask, 10 ml. of 1 *N* sodium hydroxide, and 200 mg. of manganese dioxide are added, and the mixture is heated on a steam bath for 30 min. The mixture is cooled, diluted to volume with water, mixed, and filtered. The filtrate may have to be centrifuged if it is not clear. This is the "assay solution."

Prepare and designate 2 solutions as outlined below in 50-ml. Erlenmeyer flasks:

	<i>Solution I</i>	<i>Solution II</i>
Assay solution	5 ml.	—
Isopropanol	25 ml.	25 ml.
Standard solution	—	5 ml.

Mix each of the above thoroughly and transfer two 5-ml. aliquots of Solution I to each of two 25-ml. glass-stoppered flasks labeled flask *A* and flask *B*. Transfer two 5-ml. aliquots of Solution II to each of two 25-ml. glass-stoppered flasks labeled flask *C* and flask *D*.

To flasks *A* and *C* add 1.0 ml. of ammonia buffer, 1.0 ml. of sodium acetate buffer, and 1.0 ml. of water. Cool the resulting solution to 20°C. and then add 1.0 ml. of chlorimide reagent, shake for 10 sec., and exactly 60 sec. after the addition of the chlorimide reagent, read the resulting absorbance in 1-cm. cells at 650 *mμ* versus a water blank. It is advisable to have the spectrophotometer prepared and set so that the reading of the absorbance can be made very rapidly because of the instability of the color produced.

Repeat the preceding paragraph on flasks *B* and *D* except use 1.0 ml. of boric acid solution in place of the 1.0 ml. of water.

**Calculations.**—

$$\frac{A_{650} \text{ Flask } A - A_{660} \text{ Flask } B}{A_{650} \text{ Flask } C - A_{660} \text{ Flask } D} \times 10 = \left\{ \begin{array}{l} \mu\text{g. of pyridoxine hydrochloride per} \\ \text{milliliter of "assay solution"} \end{array} \right.$$

## VITAMIN B<sub>12</sub>

Cyanocobalamin, LLD Factor



mol. wt. 1355.4

Vitamin B<sub>12</sub> is found in significant quantities in liver, spleen, kidneys, and other animal organs. Certain microorganisms produce vitamin B<sub>12</sub>, and this process is



used for the commercial production. The existence of vitamin B<sub>12</sub> was discovered only recently, in 1948<sup>78</sup>

Vitamin B<sub>12</sub> occurs as dark red, hygroscopic crystals. It absorbs about 12% of water, and, as the hydrate, it is stable in air. It is slowly decomposed by ultra violet, or by strong visible light. The cyano group attached to cobalt can be replaced by some other groups giving rise to compounds such as hydroxocobalamin, aquocobalamin, nitrocobalamin, thiocyanatocobalamin, etc. Other portions of the molecule are found altered in nature, and some of the best known of these are pseudovitamin B<sub>12</sub>, Factor A, B, C, etc.

One g is soluble in 80 ml of water; it is soluble in ethanol and phenol, but is insoluble in acetone, ether, and chloroform. On heating it darkens at 210°C but does not melt even at 300°C. Its optical rotation is  $[\alpha]_{586}^{23} = -59^{\circ}$  ( $\pm 9^{\circ}$ ) in water.

### DETERMINATION OF VITAMIN B<sub>12</sub>

The most sensitive methods for the determination of vitamin B<sub>12</sub> are microbiological methods that depend on the stimulation of the growth of microorganisms by cyanocobalamin. Several species of microorganisms are in use. USP XVI uses *Lactobacillus Leichmanni* (American type culture collection No 7830)<sup>79</sup>. Some methods use *Escherichia coli*,<sup>80</sup> *Euglena gracilis*,<sup>81</sup> or *Poterochromonas stipitata*.<sup>82</sup>

A chemical assay for cyanocobalamin is based upon the liberation of the -CN group by photolysis or chemical reduction, and the released cyanide is determined colorimetrically.<sup>83</sup>

Another method, the dicyanide assay,<sup>84</sup> is based upon the difference between the visible spectrum of cyanocobalamin and its purple dicyanide complex formed upon treating with an excess of cyanide.

### SPECTROPHOTOMETRIC METHOD

A water solution of vitamin B<sub>12</sub> shows absorption maxima at 278, 361, and 550 mμ. The ratio A<sub>361</sub>/A<sub>278</sub> is between 1.70 and 1.90, and the ratio A<sub>361</sub>/A<sub>550</sub> is between 3.15 and 3.40. In the USP XVI method, the absorption at 361 mμ of a 30 μg per milliliter solution in water is compared to cyanocobalamin reference standard at the same concentration. A correction is made for the moisture of the sample. This method can be used only for known pure cyanocobalamin, since other colored materials, many of the vitamin B<sub>12</sub> analogues, and hydrolysis or oxidation products of vitamin B<sub>12</sub>, will interfere.

### RADIOISOTOPE TRACER ASSAY

USP XV, first supplement, used this assay, which included a selective extraction and absorption, and was very specific for cobalamins that are convertible to cyanocobalamin. The present NF XI now includes this assay, and the one presented here is a modified official method. The method can be used to measure cyanocobalamin in low potency materials. Quantitative extraction of the cyanocobalamin is not necessary as long as some material in a pure form is extracted. The

<sup>78</sup> Rickes, E., Science, 107, 396, 1948.

<sup>79</sup> Shozo, M., Science, 107, 397, 1948.

<sup>80</sup> Davis, B., et al., J. Bact., 60, 17, 1950.

<sup>81</sup> Hunter, S., et al., Proc. Soc. Exp. Biol. Med., 70, 118, 1949.

<sup>82</sup> Mucke, D., et al., Die Pharmazie, 6, 305, 1960.

<sup>83</sup> Boxer, G., et al., Arch. Biochem., 30, 372, 1951.

<sup>84</sup> Rudkin, G., et al., Anal. Chem., 24, 1155, 1952.

fraction of the original cyanocobalamin recovered is determined by use of tracer cyanocobalamin containing  $\text{Co}^{60}$ , and this recovery factor permits the calculation of the cyanocobalamin contained in the unpurified sample. The method presented is a general method, and for specific problem assays, the quantities of the various extraction solutions and reagents may have to be changed to accommodate the sample. The conditions of the assay should be adjusted so that the recovery of added  $\text{Co}^{60}$  cobalamin will be at least 15%, and preferably 25% or more.

**Reagents.** Cyanocobalamin Tracer Reagent.—Dilute an accurately measured volume of standardized radioactive cyanocobalamin with sufficient water, containing 1% of benzyl alcohol, to yield a solution having a radioactivity approximately 4000 to 6000 counts per minute per milliliter. Determine the radioactivity of this reagent by measurement of 1.0 ml. in a well-type scintillation counter. Store in a refrigerator.

**Standardization.**—Prepare a solution in water, of a weighed quantity of U.S.P. cyanocobalamin reference standard to contain between 20  $\mu\text{g.}$  and 40 $\mu\text{g.}$  (preferably 30  $\mu\text{g.}$ ) in each milliliter. To determine the degree of recovery of a known amount of cyanocobalamin, perform the entire assay on a 10-ml. portion of this solution, proceeding as directed under "Assay Preparation," below, beginning with "Add water to make a measured volume. . . ." Calculate the recovery factor,  $F$ , by the formula  $(50 \times A_{361}) / (0.207 \times E \times R)$ , in which  $R$  is the quantity, in micrograms, of U.S.P. cyanocobalamin reference standard in the portion of the solution taken, and  $E$  is as defined below under "Calculation."

**Cresol-Carbon Tetrachloride Solution.**—Mix equal volumes of carbon tetrachloride and freshly distilled cresol.

**Phosphate-Cyanide Solution.**—Dissolve 100 mg. of potassium cyanide in 1000 ml. of a saturated solution of dibasic sodium phosphate, and mix well.

**Butanol-Benzalkonium Chloride Solution.**—Mix 1 volume of a 12.8% solution of butanalkonium chloride with 9 volumes of *n*-butyl alcohol.

**Determination.** Alumina-Resin Column.—Place a pledget of glass wool in the bottom of a constricted glass tube, such as a 50-ml. buret. With the tube held in an upright position, add a volume of a slurry of Amberlite IRA-401 in water, sufficient to give a column of settled resin 8 cm. in height. After the column has settled, with the aid of light tapping under 7 to 8 cm. of water, add a volume of a slurry of Amberlite MB-1 in water, sufficient to increase the height of the column an additional 7 cm. When the solid has settled somewhat, allow the water to drain so that there is only 1 cm. of liquid above the resin column, and tamp the resin lightly. Add a pledget of glass wool; then add a volume of a slurry of alumina in water, sufficient to increase the height of the settled column to 18 cm., and allow the water to drain to about 1 cm. from the top of the alumina. Add a pledget of glass wool and wash the column, using a total of 50 ml. of water, again draining to within 1 cm. of the top of the column. Prepare a fresh column for each determination. (Alumina is aluminum oxide, acid washed, reagent, chromatographic grade, having a pH of 3.0 to 5.0 in a 10 to 100 slurry.)

**Assay Preparation.**—Transfer to a beaker a weighed quantity or measured volume of the preparation to be assayed, equivalent in vitamin  $\text{B}_{12}$  activity to that of about 300  $\mu\text{g.}$  of cyanocobalamin. Add water to make a measured volume of not less than 50 ml.; then add 5.0 ml. of cyanocobalamin tracer reagent. Add, while working under a hood, 1 ml. of a 25% solution of sodium nitrite and 1 ml. of a 10% solution of potassium cyanide for each 50 ml. of resulting solution. Adjust

the solution to approximately pH 4 with diluted hydrochloric acid and heat on a steam bath for 15 min. Cool and adjust the pH to between 7.6 and 8.0 with sodium hydroxide (4.3 to 100). Centrifuge or filter to remove any undissolved solids. This constitutes the assay solution.

**Assay Procedure.**—Transfer the assay solution prepared above to a 125 ml separator and add 10 ml of cresol carbon tetrachloride solution. Shake vigorously for 2 to 5 min and centrifuge. Remove and save the lower solvent layer. Repeat the extraction using a 5 ml portion of cresol carbon tetrachloride solution and combine the lower solvent layer extracts in a separator of 125 ml capacity.

Wash the combined extracts with successive 10 ml portions of dilute sulfuric acid (1 in 7) until the last washing is practically colorless (2 washings usually suffice). During each washing shake for 2 to 5 min, allow the layers to separate, centrifuge if necessary and discard the acid layer. Wash further with 2 successive 10 ml portions of phosphate cyanide solution. Finally wash with 10 ml of water. Discard all of the washings.

To the washed extract add 30 ml of a mixture of 2 volumes of butanol benzalkonium chloride solution and 1 volume of carbon tetrachloride. Extract with 2 successive 5 ml portions of water each time shaking vigorously for 1 min. Centrifuge, remove and save the upper aqueous layer.

Pass the combined aqueous extracts through the alumina resin column at a rate of about 1 ml per minute maintaining a 1 cm layer of liquid on the head of the column by adding water as needed. Discard as much of the forerun as is colorless (usually about 5 ml) and collect the colored eluate, usually about 10 ml in a 50 ml centrifuge tube or separator containing 0.5 ml of diluted acetic acid. Extract the eluate by shaking for 2 to 5 min with 5 ml of cresol carbon tetrachloride solution and discard the upper aqueous layer. To the extract add 5.0 ml of water, 5 ml of carbon tetrachloride and 10 ml of *n*-butanol. Shake, allow to separate until the upper layer is clear and remove the upper aqueous layer.

Determine the absorbance of the aqueous extract at 361  $m\mu$  and at 550  $m\mu$  in a spectrophotometer suitable for measurements in the ultraviolet region using a tungsten light source. Make the 361  $m\mu$  reading using a filter capable of reducing stray light. Calculate the ratio of  $A_{361}/A_{550}$ , the purity of the aqueous extract is acceptable if the ratio is not less than 3.15 and not more than 3.40. If a ratio outside this range is observed, purify the aqueous extract by repeating the extraction cycle proceeding as directed in the preceding paragraph beginning with: Pass the combined aqueous extracts through the alumina resin column and using a fresh column.

If an acceptable absorbance ratio is observed in the aqueous extract, transfer 1.0 ml of it to a suitable counting tube. Add 1.0 ml of cyanocobalamin tracer reagent to another counting tube.

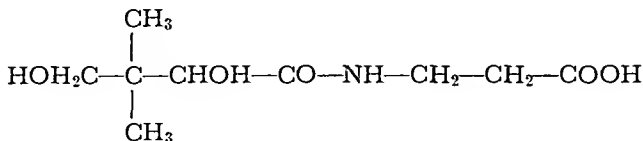
Measure the radioactivity of the contents of each counting tube in a well type scintillation counter for 5 min. Correct for observed background radioactivity determined over a 30 min period.

**Calculation.**—Calculate the efficiency  $E$  of the extraction process by the formula  $E = (C_s - C_b)/(C_r - C_b)$  in which  $C_s$  and  $C_r$  are the average radioactivity counts per minute for the preparation under assay and the cyanocobalamin tracer reagent respectively and  $C_b$  is the average count per minute of the background. The cobalamin content expressed in micrograms of cyanocobalamin of the portion taken

for assay, is given by the formula  $(50 \times A_{361}) / (0.207 \times E \times F)$ , in which  $F$  is the recovery factor calculated in the standardization of the cyanocobalamin tracer reagent.

## PANTOTHENIC ACID

Vitamin B<sub>5</sub>



C<sub>9</sub>H<sub>17</sub>NO<sub>5</sub>

mol. wt. 219.23

Pantothenic acid is widely distributed in animal and plant worlds. Especially rich in pantothenic acid are liver and molasses. The naturally occurring dextro-rotatory form is the only one having biological activity. It is synthesized by many molds and microorganisms.

**Pantothenic Acid.**—This acid is a colorless, viscous oil, quite unstable, and very hygroscopic. It is freely soluble in water, glacial acetic acid, and ethyl acetate, and slightly soluble in ether; it is insoluble in benzene and chloroform.  $[\alpha]_D^{25} = +37.5^\circ$  (water). It is sensitive to acids, alkalies, and heat.

**Sodium Pantothenate.**—C<sub>9</sub>H<sub>16</sub>NO<sub>5</sub>Na, is in the form of very hygroscopic crystals that melt at about 123°C.

**Calcium Pantothenate.**—(C<sub>9</sub>H<sub>16</sub>NO<sub>5</sub>)<sub>2</sub>Ca, mol. wt. 476.55, is reasonably stable in air, and is, therefore, the form most used in pharmaceutical formulations. It is a white, slightly hygroscopic, odorless powder with an initial sweet taste, later turning bitter. It is very soluble in water, soluble in glycerol, slightly soluble in ethanol and acetone. A 5% aqueous solution has a pH of 7.5 to 8.0. It is most stable in slightly acid solutions.  $[\alpha]_D^{25} = +28.2^\circ$  (water). A deep blue color is produced if 1 drop of 10% cupric sulfate is added to a sodium hydroxide solution of calcium pantothenate.

**Panthenol.**—Pantothenic alcohol, C<sub>9</sub>H<sub>19</sub>NO<sub>4</sub>, mol. wt. 205.25, is usually more stable than salts of pantothenic acid in an optimum pH range of 3 to 5.0. It is a viscous liquid, freely soluble in water, methanol, and ethanol, slightly soluble in ether.  $[\alpha]_D^{20} = +29.5^\circ$  (C = 5 in water). Colorimetric methods do not differentiate between racemic forms of pantothenates of which the levorotatory form is biologically inactive.

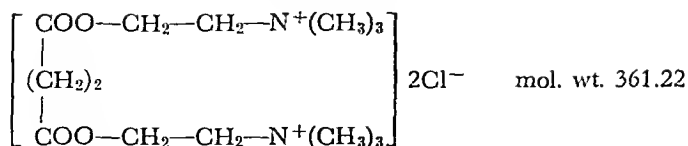
The method of E. Wollish<sup>85</sup> is based upon the formation of pantoyl lactone and *beta*-alanine after hydrolysis in acid medium. The lactone reacts with hydroxylamine in the presence of alkali, forming a hydroxamic acid, which, in turn, produces a purple color in the presence of ferric chloride.

Some of the methods are based upon the reaction of the *beta*-alanine formed after the hydrolytic cleavage.<sup>86, 87</sup>

<sup>85</sup> Wollish, E., *et al.*, *Anal. Chem.*, **22**, 1033, 1950.

<sup>86</sup> Frost, D., *Ind. Eng. Chem., Anal. Ed.*, **15**, 306, 1943.

<sup>87</sup> Szalkowsky, C., *Cereal Chem.*, **28**, 218, 1951.



White crystalline, hygroscopic powder; very soluble in water, insoluble in ether. It melts between 160° and 164°C.

**Choline Bitartrate.**— $[(\text{CH}_3)_3\text{N}^+-\text{CH}_2-\text{CH}_2\text{OH}]\text{HC}_4\text{H}_4\text{O}_6^-$ , mol. wt. 253.26. White, crystalline, and hygroscopic powder with an acidic taste. Very soluble in water, slightly soluble in ethanol, insoluble in ether.

**Choline Dihydrogen Citrate.**— $[(\text{CH}_3)_3\text{N}^+-\text{CH}_2\text{CH}_2\text{OH}]\text{H}_2\text{C}_6\text{H}_5\text{O}_7^-$ , mol. wt. 295.3. Colorless crystals, or white granular powder, hygroscopic, with an acidic taste. Very soluble in water, soluble in ethanol, very slightly soluble in ether.

Precipitation of choline by ammonium reineckate is the basis of most methods used for choline, and this basic procedure has been modified by many workers.<sup>88, 89, 90, 91</sup> Another preferred chemical method is a colorimetric periodide procedure.<sup>90</sup>

## DETERMINATION OF CHOLINE

The methodology for all choline salts is the same as that outlined below; only calculations will differ with the different salts

### REINECKATE METHOD FOR PURE MATERIALS

Accurately measure a sample equivalent to about 80 to 100 mg. of choline, and dissolve in 40 ml. of water. Add 10 ml. of a 3% filtered solution of freshly prepared ammonium reineckate to the sample, mix thoroughly, and allow to stand for 40 min. in a refrigerator. Collect the precipitate in a tared, sintered glass filter of medium porosity, and wash the precipitate with three 5-ml. portions of ice cold water (some workers prefer to use very dilute ammonium reineckate or saturated choline reineckate solutions for washing purposes). The precipitate is then washed with two 2-ml. portions of ice cold *n*-propanol. The precipitate can then be dried at 105°C. for 1 hr. and weighed. The weight of the precipitate multiplied by 0.3304 will convert the weight of the precipitate to choline chloride, by 0.5993 will convert to choline bitartrate, and by 0.6989 will convert to choline dihydrogen citrate.

The precipitate can also be dissolved by passing three 5-ml. portions of acetone through the filter, and then diluting the acetone solutions to appropriate volumes, and reading the absorbance at 520  $\mu$  in a suitable spectrophotometer versus acetone as a reference. When using the colorimetric modification, U.S.P. choline chloride reference standard should be used to establish a calibration curve. The reproducibility of the color formed is such that only occasional standardizations have to be made after the initial calibration curve is obtained.

<sup>88</sup> Engel, R., *J. Biol. Chem.*, **144**, 701, 1942.

<sup>89</sup> Kapfhammer, J., *et al.*, *Z. Physiol. Chem.*, **191**, 179, 1930.

<sup>90</sup> Thornton, M., *et al.*, *Ind. Eng. Chem., Anal. Ed.*, **14**, 39, 1942.

<sup>91</sup> Willstaedt, H., *et al.*, *Z. Vitaminforsch.*, **18**, 25, 1946.

### REINECKATE METHOD FOR COMPLEX MIXTURES AND LIVER PREPARATIONS

Heat 1 g of liver concentrate or samples equivalent to about 10 to 15 mg. of choline with 15 ml of a saturated solution of barium hydroxide for 2 hr on a steam bath in a 50 ml beaker covered by a watch glass. Neutralize the solution with glacial acetic acid and then add a saturated solution of trisodium phosphate while stirring until the sample is made strongly basic. Centrifuge the sample for about 15 min and transfer the supernatant solution quantitatively to a 25 ml volumetric flask. Dilute to volume with water and mix thoroughly. Transfer a 10 ml aliquot to a test tube add 5 ml of freshly prepared and filtered ammonium reineckate solution (3 in 100) shake the mixture vigorously and allow to stand for 40 min in a refrigerator.

Collect and wash the precipitate as in the method for pure materials above. The washed precipitate is dissolved in three 5 ml portions of acetone with the acetone solution being collected in a test tube placed over the stem of the funnel in the suction flask. Transfer the acetone solution to a 25 ml volumetric flask add sufficient acetone rinsing the test tube to make the solution measure 25 ml and mix thoroughly.

Determine the absorbance of the acetone solution of the choline reineckate in 1 cm cells using a suitable direct reading spectrophotometer set at 520  $m\mu$  and using acetone as a reference solution. Compare this absorbance with that of a USP choline chloride reference standard solution put through the procedure above.

### METHOD FOR TISSUE LIVER HOMOGENATES AND OTHER BIOLOGICAL SAMPLES

A new method that appears to have many advantages over existing methods and should be worthy of further evaluation and possible adoption as a standard method is that of Ackerman and Chou<sup>92</sup> in which the sample is homogenized in 0.15 M tris (hydroxymethyl) amino methane hydrochloric acid buffer at pH 7.4. The sample is then hydrolyzed in concentrated nitric acid for 2½ hr. After making the sample basic with sodium hydroxide the choline is precipitated with methanol c ammonium reineckate. The precipitate is washed with *n* propanol and dried. The dried precipitate is dissolved in concentrated ammonium hydroxide and then diluted with an equal volume of water and measured at 303  $m\mu$ . The authors report the method to be both sensitive and specific and able to measure all choline except that present as *o* phosphocholine. Verification of the method was made using choline methyl C<sup>14</sup> bromide. Thirteen replicates of a single homogenate assaying 133.8  $\mu$ g per milliliter had a standard deviation of  $\pm 3.6$   $\mu$ g per milliliter using aliquots equivalent to 26 to 275  $\mu$ g of choline.

### PERIODIDE METHOD

Many workers have used the method of Erickson et al<sup>93</sup> for the determination of choline in blood tissues and other products. In this method choline is precipitated with iodine as the periodide the precipitate is separated and the periodide is decomposed and converted to iodate by bromine. The iodate is titrated

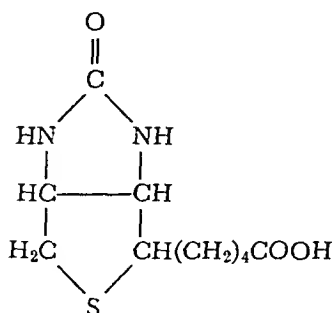
<sup>92</sup> Ackerman C J and Chou May Anal Biochem 1, 337 1960

<sup>93</sup> Erickson B et al J Biol Chem 135, 671 1940

with sodium thiosulfate. It would appear that the method of Ackerman and Chou, because of its specificity and sensitivity, would be preferable to this method.

## BIOTIN

Vitamin H      Coenzyme R



$C_{10}H_{16}N_2O_3S$

mol. wt. 244.31

Biotin was isolated from egg yolk in the form of the crystalline methyl ester. It is now believed to be present in minute amounts in every living cell. Other sources from which biotin has been isolated include liver, milk, and yeast. There are 2 known configurations of biotin, *alpha*-biotin, as found in egg yolk, and *beta*-biotin, as found in liver or milk.

*beta*-Biotin is a white, crystalline compound, slightly soluble in water, more soluble in hot water, dilute alkali, or alcohol, but insoluble in other common organic solvents. M.p.  $232^\circ$  to  $233^\circ\text{C}$ .  $[\alpha]_D^{21} = +91^\circ$  ( $C = 1$  in 0.1 *N* sodium hydroxide). It is relatively stable even in solution.

The methyl ester of biotin is a crystalline compound with a m.p. of  $166^\circ\text{C}$ . It is slightly soluble in water, soluble 1 in 100 in methanol, and soluble in acetone, ketones, benzene, etc., but insoluble in saturated or paraffin hydrocarbons.  $[\alpha]_D^{15} = +82^\circ$  (7.5 mg. in 1.28 g. methanol).

## DETERMINATION OF BIOTIN

There are no chemical methods known to be satisfactory. Biotin can be determined microbiologically using *Lactobacillus Casei*.<sup>94</sup> It can also be determined by use of *L. arabinosus*.<sup>95,96</sup> *L. arabinosus* can be used in a medium composed only of tryptophane and cystine plus vitamins and minerals.

Biotin can also be determined by the turbidimetric measurement of yeast growth.<sup>97</sup> The addition of a biotin-free casein hydrolysate<sup>98</sup> to the test medium increases the specificity of the test. The results are compared to a standard curve obtained with crystalline biotin in dilutions ranging from  $1 \times 10^{-4}$  to  $5 \times 10^{-4}$   $\mu\text{g}$ . per tube.

<sup>94</sup> Roberts, E. C., *et al.*, J. Biol. Chem., 163, 499, 1946.

<sup>95</sup> Hodson, A. Z., J. Biol. Chem., 157, 383, 1945.

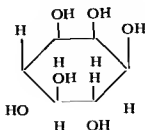
<sup>96</sup> Wright, L. D., Proc. Soc. Exp. Biol. Med., 56, 95, 1944.

<sup>97</sup> Snell, E. E., *et al.*, J. Am. Chem. Soc., 62, 175, 1940.

<sup>98</sup> Hertz, R., Proc. Soc. Exp. Biol. Med., 52, 15, 1943.

## INOSITOL

meso Inositol, Hexahydroxycyclohexane

 $C_6H_{12}O_6$ 

mol wt 180.16

Inositol, a cyclic hexa alcohol, is widely distributed in nature in both the animal and plant worlds. It is a constituent of the enzyme phytase.

Inositol is a white crystalline powder; it has a sweet taste and is optically inactive. It is soluble in water, slightly soluble in ethanol, and insoluble in ether. It melts between  $223^\circ$  and  $227^\circ\text{C}$  (anhydrous).

## DETERMINATION OF INOSITOL

## GRAVIMETRIC METHOD

For the pure substance, N F A uses a gravimetric procedure weighing the formed inositol hexaacetate.

A sample of about 200 mg is accurately weighed and transferred to a 250 ml beaker and 5 ml of a mixture of 1 part diluted sulfuric acid (1 in 20) and 50 parts acetic anhydride are added to the sample. The beaker is covered and the contents are heated on a steam bath for 20 min. The sample is removed from the steam bath, cooled in an ice bath, and carefully diluted with 100 ml of water. The diluted sample is then boiled for about 20 min, allowed to cool, and transferred quantitatively to a 250 ml separatory funnel. The solution is extracted with 30, 20, 20, 10, 10, and 10 ml portions of chloroform, rinsing the original beaker with the chloroform before each of the first 3 extractions. The extracts are collected in another 250 ml separatory funnel and washed with 10 ml of water. The washed extract is filtered through cotton into a suitable tared flask, and the separator and cotton are rinsed with additional chloroform. The chloroform extract is evaporated to dryness on a steam bath and dried at  $105^\circ\text{C}$  for 1 hr. The weight of the inositol hexaacetate obtained multiplied by 0.4167 is equivalent to the amount of inositol in the sample used for assay.

## OTHER METHODS

There are several other methods<sup>99, 100</sup> of analysis for inositol. The method of Platt and Glock<sup>101</sup> is preferable because of certain improvements in the separation of inositol from the sample. In this method inositol is oxidized with periodic acid and the excess periodic acid is determined iodometrically. The method includes

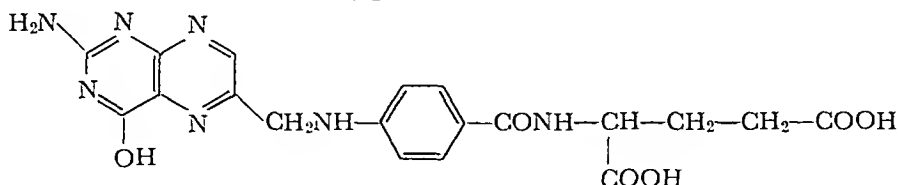
<sup>99</sup> Winter, L. B. *Biochem J.* **34**, 219 (1940).<sup>100</sup> Wooley, D. *J. Biol. Chem.* **140**, 453 (1940).<sup>101</sup> Platt, B., and Glock, G. *Biochem J.* **37**, 709 (1943).



an ion-exchange purification and a differential oxidation of inositol and of glycerol, which are usually present together. This method is designed for tissues and certain other biological samples.

## FOLIC ACID

Pteroylglutamic Acid, PGA



$C_{19}H_{19}N_7O_6$

mol. wt. 441.4

In nature there are a large number of growth factors containing pteridine or its derivative, pterioic acid. Folic acid is a conjugate of pterioic and glutamic acids. Especially rich in folic acid are liver, kidney, yeast, mushrooms, etc.

Folic acid exists as a yellowish orange, microcrystalline, odorless powder. One g. is soluble in 5000 ml. of boiling water, nearly insoluble in cold water. It is soluble in solutions of alkali hydroxides and carbonates, as well as in mineral acids. It is insoluble in acetone, ether, chloroform, and benzene. It chars at about 250°C. (no melting point).

The ratio  $A_{256}/A_{365}$  of a 1 in 6000 solution in 0.1 *N* NaOH is between 2.80 and 3.00.  $[\alpha]_D^{25} = +23^\circ$  (0.5% solution in 0.1 *N* NaOH).

## DETERMINATION OF FOLIC ACID

### COLORIMETRIC METHOD

Schiaffino *et al.*<sup>102</sup> have proposed a method based on the work of Allfrey *et al.*,<sup>103</sup> in which the folic acid is oxidized in alkaline medium to pteridine and *p*-aminobenzoic acid. The *p*-aminobenzoic acid is determined by the regular Bratton-Marshall method,<sup>104</sup> or the final colored product is extracted with isobutyl alcohol, and then measured colorimetrically. This procedure has been used both for pure folic acid and for folic acid in many pharmaceutical formulations, even those containing liver fraction and vitamin B<sub>12</sub>. The work of Schiaffino has been the source of the method now official in the U.S.P. XVI.

**Apparatus.** Spectrophotometer.—Any suitable direct reading spectrophotometer equipped with 1-cm. matched Pyrex or corex cells.

**Reagents.** Potassium Phosphate Solution.—Dissolve 30 g. of reagent grade anhydrous K<sub>2</sub>HPO<sub>4</sub> in sufficient water to make 1 liter.

Potassium Permanganate Solution.—Dissolve 20 g. of reagent grade KMnO<sub>4</sub> in water to make 500 ml. Each day before use, dilute 10 ml. of this solution to 100 ml. with water.

Sodium Nitrite Solution.—Dissolve 2.0 g. of reagent grade sodium nitrite in water to make 100 ml. Store this solution in a refrigerator.

<sup>102</sup> Schiaffino, S. S., *et al.*, J.A.Ph.A., 48, 236, 1959.

<sup>103</sup> Allfrey, V., *et al.*, J. Biol. Chem., 178, 463, 1949.

<sup>104</sup> Bratton, A., and Marshall, E., J. Biol. Chem., 128, 537, 1939.

**Ammonium Sulfamate Solution**—Dissolve 5 g of reagent grade ammonium sulfamate in water to make 100 ml. Store in a refrigerator.

**Coupling Reagent**—Dissolve 100 mg of reagent grade N (1 naphthyl) ethylene diamine dihydrochloride in water to make 100 ml. Store in a refrigerator.

**Folic Acid Stock Solution**—Weigh accurately in a dry atmosphere 50 mg of U S P folic acid reference standard that has been dried to constant weight over  $P_2O_5$ . Dissolve the standard in about 50 ml of dilute ammonium hydroxide (2 in 100) and dilute to 100 ml with the dilute ammonium hydroxide. Preserve the stock solution by adding a few drops of toluene and store in a refrigerator.

**Folic Acid Standard Solution**—Dilute 20 ml of the stock solution with potassium phosphate solution to make 100 ml. Prepare this solution fresh for each day's use. This solution contains 10  $\mu$ g of folic acid per milliliter.

**Procedure**—Transfer a measured quantity of the sample to a flask and add potassium phosphate solution so that each milliliter of solution shall contain no more than 0.1 mg of folic acid per milliliter. Heat the sample to 50° to 60° C with mixing to aid solution. The sample may have to be finely ground prior to assay if it is not readily soluble under the above conditions. Cool the solution to room temperature and dilute to a specific volume. Make any necessary dilutions with the potassium phosphate solution so the final assay solution will contain an estimated 5  $\mu$ g of folic acid per milliliter.

Duplicate determinations are made in 10 ml volumetric flasks under each of the following conditions: to a 10 ml volumetric flask labeled *A* add 20 ml of the assay solution and 2 ml of potassium phosphate solution; to flask *B* add 2 ml of assay solution, 1 ml of the standard solution and 1 ml of potassium phosphate solution; to flask *C* add 20 ml of assay solution and 2 ml of potassium phosphate solution; to flasks *A* and *B* add 1 ml of potassium permanganate solution, mix and allow to stand for 3 min; to flask *C* add 1 ml of water.

To all flasks add 1 ml of sodium nitrite solution and 1 ml of 5 N HCl solution, mix well and allow to stand for 2 min. Add to each flask 1 ml of ammonium sulfamate solution and mix thoroughly until all bubbles of  $NO_2$  are completely dispelled from the solution. Then to each flask add 1 ml of the coupling reagent and dilute to 10 ml with water. Mix thoroughly and allow to stand for 10 min.

For samples that do not contain any extraneous color other than that of the Bratton Marshall color, the absorbance is determined at 550  $m\mu$  in 1 cm cells versus water as reference.

For samples that contain extraneous color such as liver preparations etc. the final color is extracted into 10 ml of isobutyl alcohol by shaking the mixture for 2 to 3 min. The mixture is centrifuged, the clear supernatant isobutyl alcohol layer is placed in a 1 cm cell and the absorbance is determined at 550  $m\mu$  versus an isobutyl alcohol reference. The extraction and measurement of the color should be performed within 25 min after the addition of the coupling reagent.

**Calculations**—

$$\frac{\text{absorbance solution } A - \text{absorbance solution } C}{\text{absorbance solution } B - \text{absorbance solution } A} \times \frac{10}{2}$$

$$= \text{micrograms of folic acid per milliliter of assay solution}$$

**NOTE**—The folic acid can be reduced in acid solution by use of either zinc dust or a zinc mercury amalgam. Many laboratories still prefer this method and use it in place of the more recent method. Some laboratories also have had difficulty with the butanol extraction of the Bratton Marshall color and have varied the method to include more than

one butanol extraction and subsequent dilution of the butanol extract to a definite volume. In this case, it may be necessary to increase volume of sample and reagents so that the proper concentration relationship between sample and butanol extract is maintained.

#### POLAROGRAPHIC ASSAY

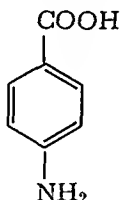
Folic acid can also be estimated polarographically, except in the presence of iron.<sup>105</sup> In the presence of 1% tetramethyl ammonium hydroxide, it has a half wave potential versus S.C.E. of 0.98 v. Using cadmium as an internal standard, the authors report an error of only  $\pm 2\%$ .

#### FLUOROMETRIC ASSAY

Allfrey *et al.*<sup>103</sup> have proposed a fluorometric assay based on the fluorescent increment before and after oxidation with permanganate. To add specificity, the oxidation product can be chromatographed on florisol, and the eluate can be measured for fluorescence in acid and base as a measure of folic acid. If there are still interferences, the eluate from the florisol column can be treated with magnasol, which adsorbs the folic acid oxidation product, and then the oxidation product is eluted from the magnasol, and the fluorescence is determined again in acid and base. This appears to be a rather promising method, worthy of further application. It has been used for natural products, but has not yet been applied to tissues.

### *p*-AMINO BENZOIC ACID

4-Aminobenzoic Acid, PABA



$C_7H_7NO_2$

mol. wt. 137.13

*p*-Aminobenzoic acid and its esters are widely distributed in nature, and are considered a growth factor for many bacteria. *p*-Aminobenzoic acid occurs as a white odorless crystalline powder (monoclinic prisms from ethanol), gradually darkening on exposure to air and light. One g. dissolves in 180 ml. of water, and in 9 ml. of boiling water. One g. of *p*-aminobenzoic acid is also soluble in 8 ml. of ethanol, and is less soluble in ether. M.p. is  $186^\circ$  to  $188^\circ C$ .  $E_{1cm}^{1\%} = 1070$  in water at 266  $m\mu$ .

### DETERMINATION OF *p*-AMINO BENZOIC ACID

#### TITRATION METHOD

*p*-Aminobenzoic acid, like related sulfanilamides and other aromatic primary amines, can be determined by reaction with nitrous acid to form a diazonium salt (diazotization).<sup>106, 107, 108</sup>

<sup>105</sup> Mader, W. J., and Frediani, H. A., *Anal. Chem.*, **12**, 1199, 1948.

<sup>106</sup> Eckert, H., *J. Biol. Chem.*, **148**, 197, 1943.

<sup>107</sup> Marshall, E., *Science*, **88**, 85, 1938.

<sup>108</sup> Ting, K., *et al.*, *J. Lab. Clin. Med.*, **34**, 822, 1949.

**Procedure**—A sample, equivalent to about 300 mg of *p* aminobenzoic acid is accurately weighed and dissolved by stirring with a mixture of 5 ml of concentrated hydrochloric acid and 50 ml of water. The solution is cooled to room temperature 20 to 30 g of crushed ice are added and the solution is slowly titrated with 0.1 *M* sodium nitrite. The end point is indicated by the production of a blue color if a drop of the solution is placed on a strip of starch iodide paper. The end of the titration is indicated only after the titrated solution has been allowed to stand for 1 min and it still produces color with the starch iodide paper.

Each milliliter of 0.1 *M* sodium nitrite is equivalent to 13.714 mg of *p* aminobenzoic acid.

### COLORIMETRIC METHOD

The *p* aminobenzoic acid content can also be determined in lower potency materials as well as blood by the Bratton Marshall method as described under Folic Acid p 2381 above. The reference standard in this case should be *p* aminobenzoic acid and a direct comparison is made.

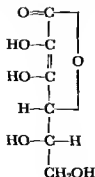
### COLORIMETRIC METHOD FOR URINE SAMPLES

Diazotized thiamine forms a color with *p* aminobenzoic acid. In the work of Kirch<sup>109</sup> the use of this reagent is discussed for the determination of *p* aminobenzoic acid in both its free and conjugated forms.

**Procedure**—Dilute about 3 ml of urine to 20 ml with water. Add 0.3 ml of glacial acetic acid and 0.1 *N* iodine until a brown color persists then add several drops of 1% sodium bisulfite solution. The pH of the mixture should be about 2.9. Add 5 ml of a solution made by mixing equal parts of 0.2% aqueous thiamine chloride with a 2% solution of sodium nitrite. Bring the pH to about 11 to 12 by the addition of 1 *N* sodium hydroxide and then add exactly 5 ml of isoamyl alcohol. By the addition of about 0.5 ml of 35% acetic acid adjust the pH to about 5.5 and shake thoroughly. Separate dry the isoamyl alcohol layer and read in a suitable spectrophotometer at about 500 mμ. This is compared to a standard of *p* aminobenzoic acid that has been treated in the same manner as the sample.

### ASCORBIC ACID

Vitamin C, L-Ascorbic Acid, Antiscorbutic Vitamin



C<sub>6</sub>H<sub>8</sub>O<sub>6</sub>

mol wt 176.13

<sup>109</sup> Kirch E. *et al.*, J Biol Chem 148, 445 1943

Ascorbic acid is widely distributed in plant and animal tissues. The most important sources of this vitamin are citrus fruits, tomatoes, ripe berries, potatoes, and many other vegetables.

Ascorbic acid is in the form of a white crystalline powder that darkens gradually on exposure to light. As a dry material it is reasonably stable in air. It has a pleasant acid taste. Ascorbic acid melts at  $191^{\circ}\text{C}$ . (decomposition), and has a  $[\alpha]_{\text{D}}^{25} = +20.5^{\circ}$  to  $+21.5^{\circ}$  (water) and  $[\alpha]_{\text{D}}^{23} = +48^{\circ}$  (methanol). One g. dissolves in 3 ml. of water, and in about 30 ml. of ethanol. It is soluble in propylene glycol and glycerol, insoluble in ether, chloroform, and benzene. A 2% solution in water has a pH of 2.4 to 2.8. It exhibits an absorption maximum at  $245\text{ m}\mu$ . A solution of ascorbic acid reduces Fehling reagent, or silver nitrate solution, and decolorizes many dyes such as 2,6-dichlorophenol-indophenol.

One of the most important chemical properties of ascorbic acid is its ability to be easily oxidized to dehydroascorbic acid,  $\text{C}_6\text{H}_6\text{O}_6$ , a neutral lactone, which is a reversibly oxidized form of ascorbic acid. Both have the same antiscorbutic activity. One U.S.P. or International unit of ascorbic acid is equivalent to 0.05 mg.

## DETERMINATION OF VITAMIN C

### IODINE TITRATION

The pure substance can be titrated with 0.1 *N* iodine in acid medium. A sample of about 300 mg. of ascorbic acid, accurately weighed, is dissolved in a mixture of 80 ml. of water and 20 ml. of diluted sulfuric acid. The solution is titrated with 0.1 *N* iodine, using 1 ml. of starch indicator, which is added near the end point of the titration. Each milliliter of 0.1 *N* iodine is equivalent to 8.806 mg. of ascorbic acid.

### POTASSIUM IODATE TITRATION

Relatively pure ascorbic acid can also be determined by titration with potassium iodate. Accurately weigh 150 to 200 mg. of ascorbic acid, and dissolve it in 10 ml. of water in a 250-ml., glass-stoppered Erlenmeyer flask. After addition of about 50 ml. of concentrated hydrochloric acid, the mixture is cooled to room temperature, and 45 ml. of 0.01 *M* potassium iodate is added from a buret. The mixture is again cooled to room temperature, 5 ml. of chloroform are added, and the mixture is shaken vigorously. The titration is continued, with continuous shaking of the flask, until the violet color in the chloroform layer completely disappears. Each milliliter of 0.01 *M* potassium iodate should be considered as equivalent to 3.523 mg. of ascorbic acid.

### 2,6-DICHLOROPHENOL-INDOPHENOL METHOD

This is probably the best known and most widely used method for the determination of ascorbic acid. Generally the method is reliable and can be used, but some knowledge of the possible interferences is essential. Any substance having a reducing potential lower than the dye would be a possible interference. Such substances would include tannins, phenols, reductones, reductone-like substances, cysteine, glutathione, and ferrous, cuprous, or stannous ion. Reduction of the dye by small amounts of many of the above can be prevented by the use of 8% acetic acid in

the extraction solution Various authors <sup>110 111, 112 113, 114</sup> have used other means of removing interferences

**Reagents.** Extracting Solution—Dissolve 15 g of metaphosphoric acid and 40 ml of glacial acetic acid in sufficient water to make 500 ml Store in a cool place This solution must be used within 2 days after it is prepared

**Standard Dichlorophenol Indophenol Solution**—To 50 mg. of 2,6 dichlorophenol indophenol sodium, which has been stored in a desiccator over soda lime add 50 ml of water containing 42 mg of sodium bicarbonate, shake vigorously, and when the dye is dissolved, dilute to 200 ml with water Filter through a No 588 (S & S) filter paper or its equivalent, into an amber, glass stoppered bottle Standardize the dichlorophenol indophenol solution as follows accurately weigh 100 mg of U S P ascorbic acid reference standard, transfer it to a 100 ml, glass stoppered volumetric flask, with the aid of sufficient extracting solution to make 100 ml at room temperature Immediately transfer 2 ml of the ascorbic acid solution to a 50 ml Erlenmeyer flask containing 5 ml of the extracting solution and titrate rapidly with the dichlorophenol indophenol solution until a distinct rose pink color persists for at least 5 sec Prepare a blank titration by titrating 7 ml of the extracting solution plus a volume of water equal to the volume of the dichlorophenol indophenol solution used in titrating the ascorbic acid solution The concentration of the standard solution is expressed in terms of its equivalent in milligrams of ascorbic acid

**Assay Procedure.**—Dissolve an amount of the sample in a sufficient amount of extracting solution so that each milliliter of solution should contain an estimated 1 mg of ascorbic acid Transfer a 2 ml aliquot to a 50 ml Erlenmeyer flask add 5 ml of the extracting solution, and titrate with the standard dichlorophenol indophenol solution until a rose pink color persists for at least 5 sec For highly colored samples it may be helpful to dilute another aliquot of the sample with water to approximately the final titrated volume, and use this as a comparison solution to detect more easily the end point color change Prepare a blank titration by titrating 6 ml of the extracting solution plus a volume of water equal to the standard dichlorophenol indophenol solution used in the above titration From the ascorbic acid equivalent of the standard dichlorophenol indophenol solution determine the ascorbic acid content of the assay solution, and account for any dilutions made during sample preparation

**Special Extraction Procedure**—If ascorbic acid is present in low concentrations as in certain food products, the following special extraction procedure should be applied blend about 200 g of a representative sample with an equal amount of the extracting solution, so that a homogeneous slurry is obtained about 20 g (or a suitable quantity to give a final concentration of about 20  $\mu$ g per milliliter) of such a slurry should be weighed into a 100 ml volumetric flask, and made up to volume using the extracting solution the sample should be filtered or centrifuged the determination of ascorbic acid can be made by titration with a standardized 2,6 dichlorophenol indophenol solution, as above, or by a photometric modification of the method as described by Bessey <sup>115</sup> and many other workers

<sup>110</sup> Gero, E. J. *Physiol et Path Gén*, **40**, 223, 1948

<sup>111</sup> Greite, D. P., and King C. G. *J Biol Chem*, **84**, 771, 1929

<sup>112</sup> Jenkins G. N. *et al*, *Proc Nutr Soc*, **3**, 124, 1945

<sup>113</sup> King, C. G., *Physiol Rev*, **16**, 238, 1936

<sup>114</sup> Lugg J. W. H., *Nature*, **150**, 577, 1942

<sup>115</sup> Bessey, O. A., *J Biol Chem*, **126**, 771 1938

*2,4-DINITROPHENYLHYDRAZINE METHOD*

This is another useful and widely used method. It was first described by J. Roe *et al.*,<sup>116,117</sup> and uses a metaphosphoric acid-acetic acid extraction of the sample. The sample is then reacted with 2% 2,4-dinitrophenylhydrazine in 9 *N* sulfuric acid. Various modifications of this method include several clean up steps. This method will measure total vitamin C, and has been used for the determination of vitamin C in blood by Lowry *et al.*<sup>118</sup>

*METHOD FOR DETERMINATION OF ASCORBIC ACID IN BLOOD*

Farmer and Abt<sup>119</sup> presented both a micro and a macro procedure based on the reaction of ascorbic acid with a standard solution of 2,6-dichlorophenol-indophenol.

For the macro procedure, 2 ml. of plasma are pipetted into a 15-ml. centrifuge tube; 4 ml. of water, and 4 ml. of 5% metaphosphoric acid are added. The contents of the tube are thoroughly mixed and centrifuged; 2 ml. of the supernatant, deproteinized plasma is pipetted into a 10-ml. test tube and titrated with a standardized 2,6-dichlorophenol-indophenol solution.

The authors state that the plasma should be deproteinized immediately, and the titration can then be made even after 24 hr.

*METHOD FOR DETERMINATION OF ASCORBIC ACID IN URINE*

In the method by L. Harris *et al.*,<sup>120</sup> the very fresh urine is titrated with a standard solution of 2,6-dichlorophenol-indophenol. If the urine cannot be titrated immediately, 10% by volume of glacial acetic acid should be added as a preservative. To an exact amount (10 ml.) of standardized 2,6-dichlorophenol-indophenol solution, acetic acid is added until a red color appears. The urine is then titrated into the solution from a 5-ml. microburet until the end point is reached.

When acetic acid is added as a preservative to urine, the necessary correction must be made in the calculation for the change in volume of the original sample.

<sup>116</sup> Roe, J. H., and Kuether, C. A., *J. Biol. Chem.*, **147**, 399, 1943.

<sup>117</sup> Roe, J. H., and Oesterling, M. J., *J. Biol. Chem.*, **152**, 511, 1944.

<sup>118</sup> Lowry, O. H., *et al.*, *J. Biol. Chem.*, **160**, 609, 1945.

<sup>119</sup> Farmer, C., and Abt, A., *Proc. Soc. Exper. Biol. Med.*, **34**, 146, 1936.

<sup>120</sup> Harris, L., and Ray, S., *The Lancet*, **228**, 71, 1935.

## Chapter 48

# WATER ANALYSIS

By Michael J. Taras

Department of Water Supply  
Detroit, Mich.

### THE PURPOSE OF CHEMICAL ANALYSIS

A chemical analysis is performed on water to ascertain its physiological or technological acceptability.

**Drinking Water**—A water that meets U. S. Public Health Service standards for drinking water satisfies the requirements of physiological acceptability. The 1961 U. S. Public Health Service drinking water standards<sup>1</sup> presented in Table 48.1 are set up in two types of limits: a limit that should not be exceeded and a limit that is cause for rejection of the water. The first limit indicates the level at which the water is likely to be objectionable to an appreciable number of people. The second limit applies to such recognized toxicants as arsenic, barium, cadmium, chromium (hexavalent), cyanide, lead, selenium, and silver. The upper limit for fluoride is predicated on the mottling effect on teeth rather than for strictly toxicological reasons.

**Water for Technological Applications**—Of the huge amount of water required daily, relatively little is consumed in drinking. The greatest volume is diverted to irrigation, cooling, and general operations in industry and homes.

Table 48.2 summarizes the instances in which chemical determinations may be performed on a water sample. In addition to appraising the public health and technological acceptability of a water, determinations become desirable whenever a chemical is applied in the course of treatment. The treatment may be as simple as chlorination or as involved as modern technology can devise. The final manufactured product largely dictates the quality to which the given supply will be treated. Only those treatments that will bring the harmful impurities to an innocuous level for the desired application are undertaken.

Enormous quantities of treated water are pressed into industrial service for cooling purposes, general plant functions, operation of steam boilers, and the direct manufacture of goods. The self-defining term "cooling water" identifies that flow that passes through condensers, furnaces, and engines. The treatment of such water may vary from intermittent chlorination to thoroughgoing completeness depending on the local situation. Water intended for drinking, flushing, and miscellaneous activities around the premises falls into the category of general purpose water. The effluent from the conventional filtration plant practicing coagulation, settling, filtration, and chlorination satisfies these requirements. High

<sup>1</sup> Hopkins, O. C. J. Am. Water Works Assn. 53, 935 and 946, 1961.



TABLE 48-1. U. S. PUBLIC HEALTH SERVICE DRINKING WATER STANDARDS (1961)

Characteristics	Limit Not to Be Exceeded	Cause for Rejection
<i>Physical Characteristics</i>		
Color	15 units	
Taste	Unobjectionable	
Threshold odor number	3	
Turbidity	5 units	
<i>Chemical Characteristics</i>		
	<i>mg. per l.</i>	<i>mg. per l.</i>
Alkyl benzenesulfonate	0.5	
Arsenic	0.01	0.05
Barium		1.0
Cadmium		0.01
Carbon chloroform extract	0.2	
Chloride	250.0	
Chromium (hexavalent)		0.05
Copper	1.0	
Cyanide	0.01	0.2
Fluoride <sup>a</sup>	0.7-1.2	1.4-2.4
Iron	0.3	
Lead		0.05
Manganese	0.05	
Nitrate (as NO <sub>3</sub> )	45.0	
Phenols	0.001	
Selenium		0.01
Silver		0.05
Sulfate	250.0	
Total solids (residue)	500.0	
Zinc	5.0	

<sup>a</sup> Variable, depending on the annual average of maximum daily air temperature. The maximum fluoride concentration applies to an air temperature of 50°F., and the minimum fluoride concentration to the temperature range of 79.3° to 90.5°F.

pressure boilers demand a pure water in the efficient production of steam for power generation, heating, and drying. Many boiler feed waters are softened by the hot or cold lime-soda, lime-sodium cation exchange, or sodium or hydrogen cation exchange process. Since silica offers serious difficulties through the formation of scale in the high-pressure boiler, as well as on the turbine blades, additional measures are adopted to minimize the SiO<sub>2</sub> concentration in the feed water.

A special quality of water is often needed to successfully manufacture a product. Some process waters must be completely demineralized by cation and anion exchangers (and in rarer instances, distilled to reduce both inorganic and organic contaminants) to be suitable for the particular application. In the food and beverage industries, the finished water is often accorded a supplementary polish by treatment with activated carbon to insure the removal of noxious tastes and odors. Waters containing soluble iron and manganese cause a yellow or reddish brown

TABLE 48-2 DETERMINATIONS PERFORMED FOR ASCERTAINING WATER QUALITY

Determinations	Public Health Acceptability	Technological (Industrial) Suitability	Control of Treatment Processes					
			Chlorination	Coagulation Settling Filtration	Softening	Boiler Treatment	Corrosion Treatment	Navigation
Physical								
Color	x	x		x			x	
pH	x	x	x	x	x	x	x	
Residue (solids)	x	x		x	x	x		
Specific conductance		x			x			
Taste and odor	x		x	x	x			
Temperature		x	x	x	x			
Turbidity	x	x		x	x		x	
Chemical								
Acidity		x		x	x	x		
Alkalinity	x	x		x	x	x	x	
Aluminum				x				
Arsenic	x							
Barium	x							
Boron		x						
Cadmium	x				x	x		
Calcium		x						
Carbon chloroform extract	x	x						
Carbon dioxide		x		x	x	x	x	
Chloride	x	x						
Chlorine (residual)	x		x					
Chlorine demand	x		x					
Chlorine dioxide	x							x
Chromium (hexavalent)	x						x	
Copper	x						x	x
Cyanide	x		x					x
Fluoride	x							
Hardness		x			x	x	x	
Iron	x	x	x	x		x	x	
Lead	x						x	
Lignin		x						
Lithium		x						
Magnesium	x	x			x	x		
Manganese	x	x	x					
Methane		x						
Nitrogen								
Albuminoid			x					
Ammonia			x					
Kjeldahl (organic)	x	x	x					
Nitrate	x						x	
Nitrite	x		x				x	
Oil and grease		x				x		
Oxygen								
Dissolved oxygen		x				x	x	
Biochemical oxygen demand	x	x						
Chemical oxygen demand		x						x
Ozone	x							
Pesticides								
Chlorinated hydrocarbon	x							
Organic phosphate	x							
Phenols	x		x					
Phosphate						x	x	
Potassium		x						
Radioactivity	x	x						
Selenium	x							
Silica		x		x		x	x	
Sodium		x			x			
Strontium		x			x			
Sulfate	x	x						
Sulfide	x		x					
Sulfite							x	
Surfactant (anionic)	x	x						
Tannin		x				x		
Zinc	x						x	

stain and deposit on contact with many objects. For this reason, an extra effort is made to remove these 2 substances from a water.

**Corrosion Control.**—The metallic construction of the pipes and equipment used to convey water and steam gives rise to the problem of corrosion. The gravity of the problem mounts with increasing heat and pressure. No simple remedy is available for combatting corrosion. At best, each solution is palliative, and applicable only to limited situations. Boiler feed water, for example, may be physically or chemically deaerated to reduce the corrosion rate in economizers, preheaters, and condensate return lines. Sodium sulfite or hydrazine is fed to boiler waters to consume chemically the residual oxygen. Raising the pH of the boiler feed water to the 9 to 11 range represents another common procedure.

A number of compounds are prescribed for curtailing corrosion in steel and cast iron water systems. These compounds, embracing ammonia, neutralizing and filming amines, and polyphosphate, are intended to produce and maintain a thin, uniform, protective film at the metallic surface. Another class of compounds is designed to inhibit the embrittlement cracking of steel by controlling the chemical composition of boiler water. Nitrate, sulfate, chloride, tannin, lignin, and other organic compounds are supposed to accomplish this objective. Sodium silicate, in combination with NaOH, is a treatment contrived for corrosive natural waters of low hardness and partially or completely softened waters in municipalities, buildings, and homes; but it is unsuitable for boiler feed waters. Chromate, silicate, polyphosphate, and such organic compounds as tannin and lignin are purported to develop thin protective films on the steel structures of circulating and aerated water systems. The deposition of a thin calcium carbonate film by regulation of the lime treatment at the municipal water plant is a method of controlling corrosion in the public water mains.

**Sanitary Analysis.**—Organic matter, ammonium compounds, albuminoid and Kjeldahl nitrogen, nitrite, and phosphate are recognized products of human or animal metabolism. Their presence in a water supply, and especially an abnormal rise over known background levels, may be considered evidence of sanitary pollution. These increases must be evaluated with respect to the total picture, however, because some industrial wastes may also be culpable.

When fewer cities and industries were situated along a water course, these chemical indicators, as well as chlorine demand and biochemical oxygen demand, had considerable significance. The growth of metropolitan areas and industrial complexes have tended to complicate the situation. The demarcation between sewage and industrial pollution is becoming less clear cut with the passage of time. Accordingly, any change from the normal values of chloride, hardness, alkalinity, and other physical and chemical characteristics of a water supply may be the result of pollution from sanitary as well as industrial sources.

## SAMPLING OF WATER

### WATER SAMPLE

The chemical components making up a water sample generally fall into 4 categories: soluble minerals; dissolved gases; soluble organic compounds; and suspended materials.

The list of soluble minerals is extensive, and likely to suffer serious omissions if a complete tabulation is attempted. However, most lists will embody the com-

mon cations calcium magnesium and sodium coupled with the anions bicarbonate sulfate and chloride

The dissolved gases found in water supplies consist of air (oxygen and nitrogen) carbon dioxide hydrogen sulfide and methane. Surface waters contain the largest amounts of dissolved oxygen and lesser concentrations of carbon dioxide and hydrogen sulfide. Methane carbon dioxide and hydrogen sulfide may occur in significant concentrations in ground waters.

The number of soluble organic materials in contemporary water supplies is growing daily through industrial synthesis. Among the common organics must be mentioned the broad group of nitrogen compounds represented by the albuminoid and Kjeldahl nitrogens together with the organic compounds that exert both a chemical and a biochemical oxygen demand. Other pollutants entering a water supply by way of sewage and industrial discharges are surfactants (synthetic detergents) phenols lignin and tannin. Many organic compounds can be adsorbed on an activated carbon filter and extracted by chloroform and are collectively identified as the carbon chloroform extract.

Despite an organic origin the color derived from the decaying vegetation of a swampy area exists largely in the form of colloidal suspensions and consequently falls into the class of suspended materials.

Natural water samples received in a laboratory for analysis often contain a solid phase in addition to the normal liquid phase. The solid phase called turbidity may range from a colloidal particle size to a coarse sand and be of inorganic or organic origin. The inorganic constituents may consist of clay silt calcium carbonate silica hydrated iron oxide alumina complex aluminosilicates and related minerals. The organic fraction may be composed of microorganisms and finely divided vegetable or animal substances of various degrees of complexity. The insoluble materials may find their way into a water supply as a result of prolonged ground contact surface run off or industrial discharges.

**Removal of Suspended Matter from Sample**—Since the ions forming the turbidity are often the same as those dissolved in the water a separation of the solid and soluble phases is important for a reliable result. Unfortunately no universally ideal method for turbidity removal is available. Each of the several methods is beset with limitations or objections therefore considerable discretion is imperative in selecting the proper method for a particular situation. Among the approaches commonly applied are centrifugation coagulation flocculation and filtrations. Coagulation with zinc sulfate and sodium hydroxide is recommended in the ammonia nitrite and nitrate determination. Flocculation with aluminum hydroxide suspension is described in the chloride nitrate and nitrite methods. Obviously coagulation and flocculation can be extended to other determinations. Filtration may be performed through papers of various textures and retentiveness through crucibles of suitable pore sizes and through cellulose acetate membranes. Centrifuging finds frequent employment but fails to match the efficiency of membrane filters for the removal of fine particles.

Filtration with the aid of zinc and aluminum hydroxide suspension activated carbon filter paper pulp and diatomaceous earth should be attempted only after their applicability has been adequately demonstrated for the given sample. The main objective in all instances is the avoidance of adsorptive losses and a consequent influence on the trace metal composition of the sample. Similarly filtration through crucibles should be undertaken only after contaminants from previous

filtrations have been eliminated. Scrupulous care should be exercised with filter papers that may contain diverse adsorbed ions.

**Compensation of Color and Turbidity in Colorimetry.**—The following measures are widely adopted in coping with small amounts of color and turbidity: (1) a parallel portion of the water sample is carried through the entire procedure except for the addition of the single color developing reagent. The solvent of the color developing reagent alone is substituted at the crucial stage. The photometer is then nulled with this sample blank; (2) the introduction of a reagent such as citric acid, which inhibits aluminum color development in the aluminon method, is another expedient that has proved beneficial; (3) bleaching the final developed color provides still another means of compensating for the background color and turbidity. Examples of this approach are the decolorization of the yellow holoquinone color of residual chlorine and *o*-tolidine by means of mercaptosuccinic (thiomalic) acid, and the discharge of the permanganate color by hydrogen peroxide in the manganese determination.

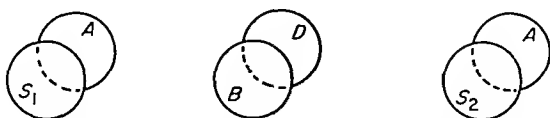


FIG. 48-1. Tube Arrangement in Block Comparator.

Figure 48-1 illustrates the arrangement of tubes by which small amounts of color and turbidity can be compensated for in visual comparisons; 2 tubes are placed one behind the other in each viewing path of the block comparator. The tubes  $S_1$  and  $S_2$  hold the lower and higher color standards, respectively, while the tubes  $A$ , immediately behind, contain the untreated water sample. Similarly, aligned alongside for comparative purposes is another pair of tubes, the first,  $B$ , holding the developed sample, and immediately behind, a tube of distilled water,  $D$ .

In the absence of color and turbidity, absorbance readings can frequently be made against a reference of a pure solvent or a reagent blank. The pure solvent may consist of distilled water, when colors are developed in aqueous solution, or the organic solvent that may be employed in extractions. The use of a pure solvent reference entails a deduction from the sample result equal to the reagent blank carried through the entire procedure. Such a correction is unnecessary when the photometric null is set with the reagent blank.

**Removal of Organic Matter Interference.**—Occasionally samples contain interfering amounts of color or organic matter that resist handling by conventional measures. The organic matter must then be destroyed by wet-ashing as described in "General Procedure for Removal of Organic Matter Interference," under "Cadmium," below, p. 2408, or by dry-ashing at temperatures not in excess of 700°C. A reagent blank should be carried through the identical procedural steps for correction purposes.

## COLLECTION OF SAMPLES

No set of instructions can possibly encompass all sampling conditions. Experience and good judgment are indispensable in these situations. Representative samples can be insured by adequately flushing a service line until the water reaches a constant temperature, before collection is attempted. The same applies to wells;

prior pumping is desirable to obtain a sample that will reflect the main body of water. Surface waters may show wide variations in sample composition with respect to depth, stream flow, or linear cross section of the river at which the collection is made. A single grab sample should be taken near the center of flow and at mid depth if the sampling program is severely restricted for any reason.

River and well samples should be collected as frequently as necessary to detect significant quality fluctuations. Local conditions and the purpose of the analysis will control the frequency and the number of diverse ions that will be determined at any treatment facility. Some laboratories save labor and expense by composing individual portions into a single sample for chemical analysis. Two distinct systems of composing may be practiced in the time-weighted method: separate portions are collected during those intervals when the water composition approximates the normal or average; in the discharge-weighted method the individual portions are combined in volumes that are proportional to the stream discharge at the time of sampling.

The collection of the sample is an important phase of the analysis. Sensible collection techniques should be observed to guarantee a sample that presents a true picture of the stream, well, reservoir, tank, basin, transmission main, or system that is being examined. The bottle should be completely filled and the stopper replaced in such a manner as to entrain as little air as possible.

Needless to say, the sooner the sample is analyzed the more reliable will be the result. In certain instances an immediate determination in the field is advisable. The determinations falling into this category are temperature, pH, residual chlorine, and dissolved gases that may be lost (oxygen, carbon dioxide, hydrogen sulfide, and methane) or gained (oxygen and carbon dioxide) in transit to the laboratory.

**Samples Containing Dissolved Gases**—Samples containing gases such as oxygen, sulfide, carbon dioxide, and methane demand special precautions for their collection in order to avert aeration, oxidation, or volatilization.<sup>2</sup> In such cases a glass or rubber tube is attached to the tap of a water line under pressure, and the water is conveyed to the bottom of the sample bottle. The water should be allowed to displace the atmosphere by a nonsplashing rise in the bottle. After the water has overflowed the bottle to the extent of several times the container capacity, sample preservation can be undertaken, or the stopper replaced in a manner to avoid air entrainment.

**Time Interval Between Collection and Analysis**—The following changes can occur in a sample when the time between collection and analysis is prolonged. Aluminum, chromium, copper, lead, and zinc may be lost through adsorption or ion exchange with the walls of a glass container. Iron and manganese may precipitate as a sediment or dissolve from the turbidity, depending on the redox potential of the sample. Sodium, silica, and boron may be leached out of a glass container. Changes in the pH-alkalinity-carbon dioxide system can induce the precipitation of calcium carbonate, thereby lowering the values for calcium and total hardness. Oxidation can cause the loss of sulfide, sulfite, nitrite, cyanide, and ferrous ion. Microbiological activity can change the nitrate-nitrite-ammonia balance, decrease the phenol content, and reduce sulfate to sulfide. Color, odor, and turbidity may increase, decrease, or change in quality. A complete list of such changes is impossible as each sampling situation bears its own peculiarities.

Because of these considerations, the physical and chemical analysis of polluted

\* Am. Public Health Assn., Am. Water Works Assn., Water Pollution Control Fed. Standard Methods for the Examination of Water and Wastewater, 11th Ed., New York, 1960.

waters should be undertaken within 12 hr. of collection, of slightly polluted waters within 48 hr., and of unpolluted waters within 72 hr.<sup>2</sup> Samples that are transported to a laboratory should, in most cases, be refrigerated and kept in the dark during shipment. Whenever an analysis must be postponed beyond the stated time limits, the sample may be pretreated or fixed to preserve a particular substance or related group of substances. The time of collection and the type of pretreatment should be recorded on the sample label.

Samples containing interfering amounts of turbidity should be freed of this turbidity before preservation. The reason for this precaution is that the fixing agent may enter into reactions with the turbidity to increase or decrease the substance under test. For example, aluminum and iron may be increased by the action of acid on turbidity, while other heavy metals and iodine may be decreased by adsorption on the suspended solids. A suitable coagulation procedure is described in "Reagents for Dissolved Sulfide," under "Sulfide," below, p. 2485.

*Procedures for Preserving Samples.*<sup>2</sup>—The following treatments have proved effective for sample preservation.

**Cyanide.**—The reactivity and instability of cyanide can be diminished by raising the sample pH to 11.0 or higher with sodium hydroxide, and refrigerating until the analysis can be undertaken as soon as possible.

**Ferrous Ion.**—The color due to ferrous ion must be developed in the field at the time of sample collection. Less than 50 ml. sample are collected in a 50-ml. bottle containing 10 ml.  $\text{NH}_4\text{C}_2\text{H}_3\text{O}_2$  buffer and 5 ml. 1,10-phenanthroline reagent, and the stopper is replaced until the solution volume can be measured and diluted to 50 or 100 ml., just prior to the final color measurement.

**Heavy Metals.**—The sample should be freed of interfering sediment, transferred to a separate, clean bottle, and acidified with concentrated HCl or  $\text{HNO}_3$  to a pH of about 3.5, to minimize precipitation and adsorption on the walls of the container of Al, Cd, Cr, Cu, Fe, Pb, Mn, and Zn.

**Nitrogen Balance (Ammonia, Albuminoid and Kjeldahl Nitrogen, and Nitrate).**—The addition of 0.8 ml. concentrated  $\text{H}_2\text{SO}_4$  to 1 liter of sample often preserves the N balance. The acid should be neutralized with NaOH or KOH immediately before the N determinations are undertaken.

**Dissolved Oxygen.**—After the clear or clarified sample has been collected with a minimum of aeration in a 300-ml., Biochemical Oxygen Demand (B.O.D.) bottle, 2 methods of preservation can be practiced on waters with little or no iodine demand.

The preferred method is to introduce in quick succession 0.7 ml. concentrated  $\text{H}_2\text{SO}_4$  and 1 ml.  $\text{NaN}_3$  solution (2 g. per 100 ml.) well below the liquid surface. The bottle is stoppered in a manner that avoids air-entrainment, mixed by inversion, and a water seal is applied to prevent the access of air. Such preservation is effective for 4 to 8 hr. at a temperature of 10° to 20°C. The determination is subsequently completed by the addition of 2 ml.  $\text{MnSO}_4$  solution, 3 ml. alkali-iodide solution, and 2 ml. concentrated  $\text{H}_2\text{SO}_4$ .

An alternative method<sup>3</sup> is to add below the liquid surface in quick succession 1 ml. KF solution, 2 ml.  $\text{MnSO}_4$  solution, and 2 ml. alkaline-iodide-azide reagent. The bottle is stoppered to avoid air-entrainment, and is mixed by inversion. After the precipitate has settled, the mixing and settling are repeated. Finally, 2 ml. concentrated  $\text{H}_2\text{SO}_4$  are run down the neck of the bottle, and the precipitate is

<sup>3</sup> Rainwater, F. H., and Thatcher, L. L., *Methods of Collection and Analysis of Water Samples*, U. S. Geological Survey Water Supply Paper 1454, 1960.

dissolved by inverting the bottle. The titration with standard 0.025  $N$   $Na_2S_2O_3$  can be delayed 2 or 3 days if the sample is refrigerated and kept in the dark.

**Phenols**—The rapid biological destruction of phenolic bodies can be retarded by the addition of 1 g  $CuSO_4 \cdot 5H_2O$  to 1 liter of sample.

**Phosphate**—Microbiological conversion of organic phosphorus to  $PO_4$  can be slowed by adding 5 ml  $CHCl_3$  to 1 liter of sample.

**Sulfide**—Sulfide samples can be preserved as long as 24 hr by precipitating  $ZnS$  along with  $Zn(OH)_2$  as a carrier. In a 250 or 500 ml bottle is placed 1 ml 1  $M$   $Zn(C_2H_3O_2)_2$  solution and the sample is collected with a minimum of aeration and splashing to a volume previously marked off on the bottle. Immediately thereafter, 1 ml 1  $N$   $NaOH$  is added and the solution is stirred for 1 to 2 min to coagulate the precipitate.

## ORDER OF ANALYSIS IN LABORATORY

The chemical determinations of unpreserved water samples transported to a distant laboratory should be undertaken in an order that accords priority to the most unstable constituents. The delicate pH-alkalinity-carbon dioxide equilibrium demands that these components should be determined immediately after the bottle is opened. Since calcium carbonate may precipitate through the loss of carbon dioxide from the opened sample, calcium hardness and dissolved residue deserve prompt attention. The walls and bottom of the container should be examined closely for evidence of  $CaCO_3$  deposition. Any solid  $CaCO_3$  can be dissolved by adding a small piece of commercial dry ice ( $CO_2$ ) or mineral acid to the sample. The specific conductance should be measured early for a valuable clue regarding the sample volumes that will be needed in subsequent determinations.

All the separate bottles containing such dissolved gases as  $CO_2$ ,  $H_2S$ ,  $CH_4$  and dissolved oxygen as well as such reductants as ferrous, nitrite and sulfite ions should be handled with dispatch in order to minimize losses due to standing and oxidation. The preserved samples for phenols, phosphate and the nitrogen balance should also receive swift action.

## PREPARATION OF COMMON INCIDENTAL REAGENTS

Some incidental reagents are administered with such frequency in water analysis that their preparation with distilled water is described here in order to conserve space in the following sections. Unless otherwise indicated, all reagents used in water analysis should meet or exceed American Chemical Society (ACS) specifications.

**Special Types of Distilled Water**—The following special types of distilled water are needed for diluting samples and preparing reagent solutions in water analysis.

**Redistilled Water**—This is distilled water that has been redistilled from an all-borosilicate glass apparatus, and then stored in a glass stoppered borosilicate container.

**Deionized Distilled Water**—To prepare, pass distilled water through an efficient column of strongly acidic cation exchange resin in the hydrogen form and a strongly basic anion exchange resin in the hydroxyl form.

**Boiled Distilled Water**—Prepare by boiling distilled water for 10 to 30 min to remove such dissolved gases as  $CO_2$  and oxygen, and cooling to room temperature immediately before use.



*Acids.*—Many methods entail the use of the desk acids listed in Table 48 3 For this reason, the ready availability of this group of reagents is strongly recommended

TABLE 48-3 PREPARATION OF ACID DILUTIONS

Acid Concentration	Volume of Concentrated Acid Needed to Prepare 1 Liter of Specified Solution		
<i>Normality</i>	36–37% <i>HCl</i> , <i>ml</i>	96–98% <i>H<sub>2</sub>SO<sub>4</sub></i> , <i>ml</i>	69–70% <i>HNO<sub>3</sub></i> , <i>ml</i>
18	—	500 or (1 + 1) <sup>a</sup>	—
6	500 or (1 + 1) <sup>a</sup>	167 or (1 + 5) <sup>a</sup>	380
1	83 or (1 + 11) <sup>a</sup>	28	64
0.1	83	28	64

<sup>a</sup> The A + B system of specifying preparatory volumes means that A volumes of the concentrated reagent are diluted with B volumes of distilled water to form the required solution

**Bases. Sodium Hydroxide Solutions.**—All NaOH solutions should be prepared from boiled, distilled water, and should be protected against contamination by tubes containing CO<sub>2</sub> absorbants

The strongest solution, 15 *N*, is prepared by carefully dissolving 625 g NaOH in 800 ml distilled water to form 1 liter of solution The Na<sub>2</sub>CO<sub>3</sub> can be removed by keeping the solution in a water bath at the boiling point for a few hours, or by allowing the solution to stand for a few days

The following volumes of 15 *N* NaOH supernatant liquid must be diluted to form 1 liter of the indicated normalities 400 ml for 6 *N*, 67 ml for 1 *N*, and 6.7 ml for 0.1 *N*

**Ammonium Hydroxide Solutions.**—The following volumes of concentrated NH<sub>4</sub>OH, approximately 15 *N*, must be diluted to form 1 liter of the indicated normalities 200 ml for 3 *N*, and 13 ml for 0.2 *N*

**Oxidants and Reductants. Potassium Permanganate Solution,** 0.10 *N*, 3.161 g per 1000 ml

**Sodium Thiosulfate Solution,** 0.10 *N*.—This stock solution is prepared by dissolving 24.819 g Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> · 5H<sub>2</sub>O in freshly boiled distilled water, diluting to 1000 ml, and preserving with 5 ml CHCl<sub>3</sub> or 0.4 g NaOH

**Indicators.**—The commercial availability of the sodium salts of many indicators enables the easy preparation of aqueous solutions of the required indicators Should the acid form of the indicator be on hand, dissolution can be accomplished in 95% ethyl or isopropyl alcohol, or the indicator can be triturated with the calculated volume of 0.05 *N* NaOH, and then diluted with distilled water

**Phenolphthalein Indicator Solution.**—This is prepared by dissolving 0.5 g in 50 ml 95% ethyl or isopropyl alcohol, adding 50 ml distilled water, and introducing 0.02 *N* NaOH drop by drop until a faint pink appears

**Methyl Orange Indicator Solution,** 0.05 g. per 100 ml.

dissolved by inverting the bottle. The titration with standard 0.025 N  $\text{Na}_2\text{S}_2\text{O}_4$  can be delayed 2 or 3 days if the sample is refrigerated and kept in the dark.

**Phenols**—The rapid biological destruction of phenolic bodies can be retarded by the addition of 1 g  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  to 1 liter of sample.

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**Boiled Distilled Water**—Prepare by boiling distilled water for 10 to 30 min to remove such dissolved gases as  $\text{CO}_2$  and oxygen and cooling to room temperature immediately before use.

**Methyl Red Indicator Solution, 0.1 g per 100 ml**

**Starch Indicator Solution**—A thin paste is formed by rubbing 0.5 g potato, arrow root or soluble starch and a few milliliters of distilled water with a stirring rod. While mixing the paste is poured into 100 ml of boiling, distilled water. The decanted supernatant liquid is preserved with any 1 of the following reagents: 0.13 g s licylic acid, 0.4 g  $\text{ZnCl}_2$ , or a combination of 0.4 g sodium propionate and 0.2 g  $\text{NaN}_3$ .

**Miscellaneous Solutions** **Sodium Bicarbonate pH 8.3 Color Standard**—This standard is prepared immediately before use by dissolving 0.1 g in 100 ml boiled distilled water. The identical volume of phenolphthalein indicator, as is specified for the given titration, is introduced into this color standard, and the solution is placed in the same size and type of white porcelain casserole or flask used for the titration of the water sample.

**Aluminum Hydroxide Suspension**—This is prepared by dissolving 125 g  $\text{K}_2\text{Al}(\text{SO}_4)_4 \cdot 24\text{H}_2\text{O}$  or  $(\text{NH}_4)_2\text{Al}(\text{SO}_4)_4 \cdot 24\text{H}_2\text{O}$  in 1 liter of distilled water, warming to  $60^\circ\text{C}$ , and slowly adding 55 ml concentrated  $\text{NH}_4\text{OH}$  with constant stirring. The precipitate is allowed to settle for 1 hr, then it is transferred to a large bottle and washed by the repeated addition, agitation, and decantation of distilled water until the rinse water remains free from  $\text{NH}_3$ , chloride, nitrate, and nitrite. When freshly prepared, the  $\text{Al}(\text{OH})_3$  floc occupies a volume of approximately 1 liter. The suspension is stored in a borosilicate glass container, and dispensed after thorough shaking.

## PHYSICAL AND CHEMICAL DETERMINATIONS

### ACIDITY<sup>2</sup>

The term 'acidity' is applied to that group of constituents that can be titrated with a strong base. The acidity titration can be conducted to the methyl orange end point of pH 4.5 if mineral acids are present or to the phenolphthalein end point of pH 8.3. These end points represent the  $\text{H}_2\text{CO}_3$  and bicarbonate equivalence points, respectively. Boiling the sample accelerates the hydrolysis of acid mine drainage wastes containing iron and aluminum sulfates. This step overcomes the fading phenolphthalein end point, which may occur when the titration is conducted at room temperature. Where the instrumentation is available, the acidity can be titrated potentiometrically. Acidity results are reported in terms of  $\text{CaCO}_3$ .

Minimal amounts of 0.1 N  $\text{Na}_2\text{S}_2\text{O}_3$  are added to the sample to remove the residual chlorine that would otherwise impair the methyl orange color changes.

**Reagents** **Boiled Distilled Water**—This should be used in the preparation of all solutions and dilutions.

**Standard Sodium Hydroxide Titrant, 0.02 N**—Dilute 20.0 ml 1 N NaOH to 1 liter with water. Standardize against 0.0200 N potassium acid phthalate under exactly the same conditions (similar volumes of final solution, 0.1 N  $\text{Na}_2\text{S}_2\text{O}_3$  and indicator solutions) as the titration of water samples. Pipet a volume of standard phthalate solution that approximates either the average or median (whichever is applicable) acidity usually prevailing in the water samples determined in the particular laboratory. The equivalence of 0.0200 N NaOH is 1.00 mg  $\text{CaCO}_3$  per 1.00 ml.

**Reagents** Boiled Distilled Water.—This should be used in the preparation of all solutions

**Standard Acid Titrant, 0.02 N**—Dilute 200 ml 0.1 N HCl or  $H_2SO_4$  to 1 liter with water. Standardize against 0.0200 N  $Na_2CO_3$  under exactly the same conditions (similar volumes of final solution 0.1 N  $Na_2S_2O_3$  and indicator solutions) under which the water samples are titrated. Pipet a volume of standard  $Na_2CO_3$  that approximates either the average or median (whichever is applicable) alkalinity usually prevailing in the water samples determined in the particular laboratory. The equivalence of 0.0200 N acid is 100 mg  $CaCO_3$  per 100 ml.

**Standard Sodium Carbonate Solution, 0.0200 N**—Dissolve 1.060 g  $Na_2CO_3$  primary standard grade (dried at 110°C.) and dilute to 1000 ml with water.

**Mixed Bromocresol Green Methyl Red Indicator Solution**—Dissolve 0.02 g sodium salt of methyl red and 0.10 g sodium salt of bromocresol green in 100 ml water.

Phenolphthalein Indicator

Methyl Orange Indicator

Sodium Bicarbonate pH 8.3 Color Standard

Sodium Thiosulfate, 0.1 N

**Procedure**—Select a sample volume (preferably 50 or 100 ml) that will require less than 25 ml titrant. Pipet the sample into a white porcelain casserole or into a flask that is handled over a white surface during the titration. Remove any free residual chlorine by adding 0.05 ml (1 drop) of 0.1 N  $Na_2S_2O_3$ .

**Phenolphthalein Alkalinity**—Add 0.1 ml (2 drops) of phenolphthalein indicator to the sample and titrate with 0.02 N standard acid to the same color as that of the pH 8.3  $NaHCO_3$  color standard. Record the buret reading and continue titrating the total alkalinity by either the mixed indicator or methyl orange method.

**Total Alkalinity by Mixed Indicator Method**\*—Add 0.15 ml (3 drops) of mixed bromocresol green methyl red indicator to the water sample, and resume the titration with 0.02 N standard acid to the following color changes: light blue with lavender gray (pH 5.0) for a total alkalinity up to 50 mg per liter of  $CaCO_3$ ; light pink gray with bluish cast (pH 4.8) for a total alkalinity up to 150 mg per liter of  $CaCO_3$ ; and light pink (pH 4.6) for a total alkalinity up to 500 mg per liter of  $CaCO_3$ .

**Total Alkalinity by Methyl Orange Indicator Method**—Add 0.1 ml (2 drops) of methyl orange indicator to the water sample, and resume the titration to the appearance of a very faint orange color.

$$\text{Phenolphthalein alkalinity as milligrams per liter of } CaCO_3 = \frac{A \times N \times 50000}{\text{milliliters of sample}}$$

$$\text{Total alkalinity as milligrams per liter of } CaCO_3 = \frac{B \times N \times 50000}{\text{milliliters of sample}}$$

where  $A$  = milliliters of titration for sample required to reach the phenolphthalein end point,

$B$  = total milliliters of titration for sample (including the titration  $A$ ) required to reach the mixed indicator or methyl orange end point, and

$N$  = normality of acid titrant

\* Cooper S. S. Ind. Eng. Chem. Anal. Ed. 13, 466 (1941)

If desired, calculate the approximate bicarbonate, carbonate, and hydroxide concentrations by the equations presented in Table 48-4.<sup>5</sup>

TABLE 48-4. RELATIONSHIPS BETWEEN ALKALINITY TITRATIONS AND BICARBONATE, CARBONATE, AND HYDROXIDE CONCENTRATIONS

Titration Results <sup>a</sup>	Hydroxide as CaCO <sub>3</sub>	Carbonate as CaCO <sub>3</sub>	Bicarbonate as CaCO <sub>3</sub>
P = 0	0	0	T
P < $\frac{1}{2}$ T	0	2P	T - 2P
P = $\frac{1}{2}$ T	0	2P	0
P > $\frac{1}{2}$ T	2P - T	2(T - P)	0
P = T	T	0	0

<sup>a</sup> P = phenolphthalein alkalinity; T = total alkalinity.

### ALUMINUM<sup>2, 6, 7</sup>

Polyphosphates, like fluoride, cause low aluminum results, and may be volatilized by the same procedure as fluoride. Polyphosphates can also be eliminated by boiling a 50- to 100-ml. sample with 4 ml. 6 N H<sub>2</sub>SO<sub>4</sub>. The negative error contributed by sulfite levels in excess of 10 mg. per liter can be corrected by oxidation with 3% H<sub>2</sub>O<sub>2</sub>. Residual chlorine concentrations above 0.5 mg. per liter should be reduced with Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>. In the presence of 1.0 mg. per liter of Al, Ca concentrations yield a positive error progressing from 0.02 mg. per liter of Al at 2.4 mg. Ca, to 0.1 mg. per liter of Al at 15 mg. Ca in the portion taken for analysis.

**Reagents. Standard Aluminum Solution.**—Prepare the stock solution containing 0.500 mg. Al per 1.00 ml. from the pure metal as described in (a), or from potassium alum as described in (b). (a) Dissolve 0.5000 g. Al in 10 ml. concentrated HCl with gentle heat, cool to room temperature, and dilute to 1000 ml. with distilled water. (b) Dissolve 8.792 g. K<sub>2</sub>Al<sub>2</sub>(SO<sub>4</sub>)<sub>4</sub> · 24H<sub>2</sub>O in distilled water, and dilute to 1000 ml. (c) Dilute 10.00 ml. stock solution (a) or (b) to 1000 ml. with distilled water, to form a standard solution containing 0.005 mg. Al per 1.00 ml. Prepare the standard solution daily.

**Aluminon-Buffer Reagent.**—Dissolve each of the following chemicals in separate 100-ml. portions distilled water, and mix the resulting solutions in the order listed: 133 g. ammonium acetate, 126 ml. concentrated HCl, 0.9 g. ammonium salt of aurin tricarboxylic acid, and 10 g. gum arabic (also called gum acacia). Dilute to 1 liter with distilled water, mix, and allow to stand overnight. Filter through fine glass wool or under suction. Store in the dark to maintain stability up to 6 months. The pH of the solution should be 3.8 to 4.0.

**Thioglycolic Acid Solution.**—Dilute 1 ml. of thioglycolic acid (also called mercaptoacetic acid) to 100 ml. with distilled water. Prepare daily.

<sup>5</sup> Table reproduced with permission from Standard Methods for the Examination of Water and Wastewater, 11th Ed., The American Public Health Assn., Inc., New York, 1960.

<sup>6</sup> Packham, R. F., Proc. Soc. Water Treatment and Examination, 7, 102, 1958.

<sup>7</sup> Shull, K. E., J. Am. Water Works Assn., 52, 779, 1960.

Citric Acid Monohydrate Solution 10 g per 100 ml

*p* Nitrophenol Indicator Solution, 1 g per 100 ml

Sulfuric Acid Concentrated

Hydrochloric Acid Concentrated

Hydrochloric Acid 1 + 11

Ammonium Hydroxide 1 + 4

Sodium Carbonate

**Procedure Preliminary Sample Treatment**—Pipet 2 portions of the sample containing less than 0.05 mg Al into 250 ml flasks. If necessary dilute to 50 ml with distilled water. Add 1 drop (0.05 ml) *p* nitrophenol indicator. Discharge any resulting yellow color by the dropwise addition of 1 + 11 HCl. If the sample remains colorless add 1 + 4  $\text{NH}_4\text{OH}$  drop by drop to produce a faint yellow color then discharge the yellow color with the dropwise addition of 1 + 11 HCl. When the sample contains color or turbidity convert the second portion into a sample blank by adding 1 ml citric acid solution.

**Color Development**—Prepare a blank and a series of Al standards in the range of 0.001 to 0.050 mg and dilute with distilled water to 50 ml in 250 ml flasks. Treat the blank and standards exactly as the sample throughout the procedure. Mixtures after each addition introduce 2 ml thio-glycolic acid solution and with a volumetric pipet 10 ml aluminum buffer reagent. Immerse all flasks in a boiling water bath for exactly 15 min making certain that the liquid level in the flasks is completely submerged in the boiling water throughout the entire period. After cooling the flasks to the temperature range 20° to 25°C transfer the contents to 100 ml volumetric flasks or Nessler tubes and dilute to the mark with distilled water. Read the absorbance at 525 m $\mu$  in a cell of 1 cm length or longer or visually match the colors in Nessler tubes. Set the photometric null of each sample with the second portion that was treated with citric acid.

**Elimination of Fluoride Interference**—Pipet the sample into a platinum dish and evaporate to dryness on a steam or water bath. Wet the entire residue with 5 ml concentrated  $\text{H}_2\text{SO}_4$  and carefully take to dryness on a hot plate or sand bath guarding against spattering. Fuse the residue with 0.5 g  $\text{Na}_2\text{CO}_3$  and allow the cake to cool. Extract first with 10 ml hot distilled water then with 5 ml concentrated HCl applying gentle heat for a few minutes. Finally add 10 ml distilled water and wash the contents of the dish into a beaker. Boil the solution for a few minutes to expel  $\text{CO}_2$  transfer to a 250 ml flask and complete the determination beginning with Preliminary Sample Treatment above. Prepare a reagent blank by dissolving 0.5 g  $\text{Na}_2\text{CO}_3$  in 40 ml distilled water and add 5 ml concentrated HCl followed by 5 ml concentrated  $\text{H}_2\text{SO}_4$  for the purpose of applying the proper Al correction.

$$\text{Al milligrams per liter} = \frac{\text{milligrams of Al} \times 1000}{\text{milliliters of sample}}$$

## ARSENIC\*

The heteropoly blue colorimetric method is adaptable for precise and accurate determinations in the presence of antimony. All glassware used in the heteropoly blue method however must be thoroughly cleansed with dilute  $\text{HNO}_3$  and rinsed with distilled water to guard against high values resulting from adsorbed  $\text{SiO}_2$  and  $\text{PO}_4$  contamination. The Guzeit method on the other hand is suitable for semi-quantitative estimations when antimony is present in amounts below 0.10 mg.

because  $\text{SbH}_3$  and  $\text{AsH}_3$  yield similar stains on  $\text{HgBr}_2$  paper. Both methods require considerable practice for successful execution, and care should be exercised in the addition of reagent volumes.

**Reagents.** Standard Arsenic Solution.—(a) Dissolve 0.1320 g.  $\text{As}_2\text{O}_3$ , dried at  $105^\circ\text{C}$ ., in a minimum volume (approximately 10 ml.) of 1 *N* NaOH. Neutralize with 1 *N*  $\text{H}_2\text{SO}_4$ , and dilute to 1000 ml. with distilled water.

(b) Dilute 10.00 ml. stock solution to the mark of a 100-ml. volumetric flask with distilled water to form a standard solution containing 0.010 mg. As per 1.00 ml.

Stannous Chloride Reagent.—Dissolve 40 g.  $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$  in 25 ml. concentrated HCl, and dilute to 100 ml. with distilled water.

Potassium Iodide Solution, 15 g. per 100 ml.—Store in a brown bottle, and discard upon development of a decided yellow color.

Sodium Hypobromite Solution.—Add 2 ml. bromine to 470 ml. distilled water in a brown, glass-stoppered bottle, then add 30 ml. 6 *N* NaOH, and immediately shake well until the bromine dissolves.

Lead Acetate Solution.—Ten g.  $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot 3\text{H}_2\text{O}$  per 100 ml.

Zinc, 20 to 30 mesh. As-free.

Roll of Dentist's Cotton.—Cut into 25-mm. lengths.

Nitric Acid, Concentrated.

Sulfuric Acid, 1 + 1.

**Reagents for Heteropoly Blue Colorimetric Method.** Ammonium Molybdate Reagent.—(a) Add cautiously 310 ml. concentrated  $\text{H}_2\text{SO}_4$  to 400 ml. distilled water. (b) Dissolve 50 g.  $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$  in 200 ml. distilled water. (c) After solution (a) has cooled, add it to solution (b), and dilute to 1 liter.

Hydrazine Sulfate Solution, 1.5 g. per 100 ml.

Sulfuric Acid, 1 *N*.

**Reagents for Gutzeit Semiquantitative Method.** Mercuric Bromide Paper.—For convenience, secure commercial arsenic strips cut into strips 2.5 mm. wide and 12 to 18 cm. long. Immerse the strips for at least 1 hr. in a filtered solution prepared by dissolving 3 to 6 g.  $\text{HgBr}_2$  in 95% ethyl or isopropyl alcohol. Dry the soaked strips by waving in the air. Sensitize the strips in this manner just prior to need, and store no longer than 2 hr. before use.

**Procedure.**—Select a sample volume containing 0.01 to 0.04 mg. As. In the case of a potable water meeting USPHS drinking water standards for As, add 7 ml. 1 + 1  $\text{H}_2\text{SO}_4$  and 5 ml. concentrated  $\text{HNO}_3$  to a 1000-ml. sample, and evaporate to  $\text{SO}_3$  fumes. To prevent As reduction and loss, maintain an excess of  $\text{HNO}_3$  until the organic matter is destroyed, and do not allow the solution to darken from the decomposition of the organic matter. Add 25 ml. distilled water to the cooled concentrate, and again evaporate to  $\text{SO}_3$  fumes to remove the oxides of nitrogen. Dilute the cooled concentrate to 25 ml. with distilled water.

Impregnate one end of the 2.5-cm. length of cotton with  $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2$  solution, and insert in the glass guard column, *B*, as shown in Figs. 48-2 and 48-3. Continue the procedure from this point by the heteropoly blue colorimetric method or the Gutzeit semiquantitative method.

**Heteropoly Blue Colorimetric Method Finish.**—Place glass beads of 2- to 3-mm. diameter size in the absorption tube (*C* in Fig. 48-2) to a height of 7.5 cm., and wet with 3 ml. NaOBr solution.

Transfer the 25-ml. diluted concentrate to the Gutzeit generator (*A* in Fig. 48-2). Add 7 ml. 1 + 1  $\text{H}_2\text{SO}_4$  and cool. Add 5 ml. KI solution, 4 drops (0.20 ml.)  $\text{SnCl}_2$  reagent, and 2 to 5 g. Zn; and immediately connect the absorption tube with the

generator. Immerse the generator in a water bath maintained at 20° to 25°C for 1 to 1½ hr. Wash the contents of the absorption tube into a 25 ml matched 16 by 150 mm test tube with six 2 ml portions distilled water.

Prepare the following standards in matched 16 by 150 mm test tubes 0.000,

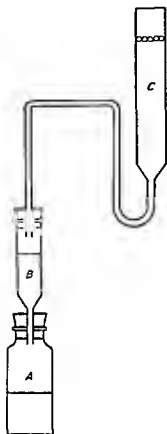


FIG 48.2 Apparatus for Heteropoly Blue Colorimetric Method (Reproduced with permission from Standard Methods for the Examination of Water and Wastewater 11th Ed. The American Public Health Assn Inc New York 1960)



FIG 48.3 Apparatus for Gutzeit Semi-quantitative Method (Reproduced with permission from Standard Methods for the Examination of Water and Wastewater 11th Ed. The American Public Health Assn Inc New York 1960)

0.010, 0.020, 0.030, and 0.010 mg As. Add 3 ml  $\text{NaOBr}$  solution and dilute with distilled water to 15 ml. Thereafter treat the blank and standards exactly as the sample throughout the remaining procedure.

Mixing after each addition introduce 5 ml 1 N  $\text{H}_2\text{SO}_4$ , 1.00 ml (volumetric pipet) ammonium molybdate reagent and 1.0 ml  $\text{N}_2\text{H}_4 \cdot \text{H}_2\text{SO}_4$  solution. Dilute to 25 ml with distilled water and mix. After 1 hr visually match the developed color against temporary standards or read the absorbance at 820 m $\mu$  preferably.



or at 650  $m\mu$  in a spectrophotometer, or at 600 to 820  $m\mu$  in a filter photometer, using a cell of 1-cm. length or longer.

**Gutzeit Semiquantitative Method Finish.**—Restore the dried narrow glass tube (C in Fig. 48-3) to its proper position, and introduce the  $HgBr_2$  test paper, making certain that the paper strip is straight.

Transfer the 25-ml. diluted concentrate to the Gutzeit generator (A in Fig. 48-3). Add 7 ml. 1 + 1  $H_2SO_4$  and cool. Add 5 ml. KI solution, 4 drops (0.20 ml.)  $SnCl_2$  reagent, and 2 to 5 g. Zn; and immediately replace the absorption tube over the generator. Immerse the generator in a water bath maintained at 20° to 25°C. for 1½ hr. Remove the paper strip, measure the lengths of the stains on both sides, and take the average of the 2 lengths. Estimate the As concentration from a calibration curve prepared by subjecting a reagent blank and standards to the same evolution procedure. Space the standards at 0.005-mg. intervals in the 0 to 0.030-mg. As range. Change the amount of 1 + 1  $H_2SO_4$  to 14 ml. (instead of 7 ml.), however, in the 25-ml. volume of the blank and standards.

$$\text{As, milligrams per liter} = \frac{\text{milligrams of As} \times 1000}{\text{milliliters of sample}}$$

## BORON

The potentiometric method is recommended for waters of high boron content, where accuracy is important. It is also applicable in the B range of 0.10 to 5 mg. per liter, while the carmine method is suitable for the B range of 1 to 10 mg. per liter. Both methods can be extended beyond these limits by concentrating or diluting the original sample.

Samples and reagents should be stored in polyethylene containers or alkali-resistant, boron-free glassware to minimize boron pick-up.

### POTENTIOMETRIC METHOD<sup>2,8</sup>

Phosphate concentrations over 10 mg. per liter and such weak ions as  $CO_3$ ,  $NH_4$ , Fe, and Al, which may buffer the sample, interfere. Precautions should be taken during the titration against the pH drift possible by the absorption of acidic or alkaline fumes in the laboratory atmosphere.

**Reagents.** Boiled Distilled Water.—This should be used in the preparation of all solutions.

**Standard Sodium Hydroxide Titrant, 0.0231 N.**—Dilute 46 ml. of 0.5 N NaOH to 950 ml. with water. Pipet volumes of 2-, 5-, and 10-ml. of standard  $H_3BO_3$  solution, dilute to 250 ml., and standardize the NaOH daily by following the complete boron procedure. Adjust the solution to the proper normality. The equivalence of 0.0231 N NaOH is 0.250 mg. boron per 1.00 ml.

**Standard Boron Solution.**—Dissolve 0.5716 g.  $H_3BO_3$ , dried in a desiccator, in distilled water, and dilute to 1000 ml. to form a solution containing 0.100 mg. boron per 1.00 ml. Do not dry the  $H_3BO_3$  at 105°C., but use a chemical that meets ACS specifications, which has been tightly stoppered, to prevent absorption of atmospheric moisture.

**Methyl Red Indicator.**

**Standard Buffer Solution, pH 7.00.**

**Sulfuric Acid, 1 N.**

<sup>8</sup> Wilcox, L. V., Ind. Eng. Chem., Anal. Ed., 12, 341, 1940.

Sodium Hydroxide 1 N

Mannitol (Boron Free)

**Procedure**—Place a sample volume containing less than 1 mg B in a 400 ml tall form or a 600 ml beaker. Dilute to 250 ml if a smaller aliquot has been taken. Acidify to methyl red indicator (3 to 5 drops) then add 0.5 to 1.0 ml 1 N  $\text{H}_2\text{SO}_4$  in excess. Bring to a boil stir cautiously at first then vigorously to expel the  $\text{CO}_2$ . Cover the beaker and rapidly cool to room temperature preferably in a water bath. (Add more 1 N  $\text{H}_2\text{SO}_4$  if boiling results in a return of the alkaline indicator color.) Adjust the pH meter to pH 7.00 with a standard buffer solution. Wash the glass and calomel reference electrodes thoroughly with distilled water and insert the electrodes into the sample. Stirring the sample gently throughout the entire titration first raise the pH to approximately 5.0 by adding carbonate free 1 N  $\text{NaOH}$  then add the standard 0.0231 N  $\text{NaOH}$  until the pH is exactly 7.00. Record the buret reading and add  $5 \pm 0.1$  g mannitol. (The presence of B in the sample will cause the pH to drop below 7.00 at this point.) Rapidly titrate with standard 0.0231 N  $\text{NaOH}$  until the pH is again exactly 7.00 and record the second buret reading. Carry a 250 ml blank of boiled distilled water through the complete procedure.

$$\text{B milligrams per liter} = \frac{(A - C) \times D \times 1000}{\text{milliliters of sample}}$$

where A = milliliters of titration for sample

C = milliliters of titration for blank and

D = milligrams of B equivalent to 1.00 ml of 0.0231 N  $\text{NaOH}$

#### CARMINE COLORIMETRIC METHOD<sup>2</sup>

The ions present in most potable waters seldom interfere at the customary levels. Silica interference varies with the B concentration. At 0.5 mg per liter of B the result may be approximately 20% high in the presence of 5 or 30 mg per liter of  $\text{SiO}_2$  and may fluctuate at lower B levels. Fluoride  $\text{NO}_3$  and  $\text{PO}_4$  concentrations exceeding those normally encountered in drinking supplies interfere to a lesser extent.

**Reagents** Standard Boron Solution—Prepare as described in Potentiometric Method under Boron above.

**Carminic Acid Reagent**—5.0 g carminic acid NF 40 or carminic acid in 1 liter concentrated  $\text{H}_2\text{SO}_4$  until dissolved. Check the calibration curve daily to keep abreast of the reagent's deterioration.

Sulfuric Acid Concentrated

Hydrochloric Acid Concentrated

Hydrochloric Acid 1 + 11

Sodium Hydroxide 1 N

**Procedure** Preliminary Sample Treatment—If the sample contains less than 1 mg per liter of B pipet an aliquot containing 0.002 to 0.02 mg B into a platinum dish make alkaline with 1 N  $\text{NaOH}$  plus a slight excess and evaporate to dryness on a steam or water bath. If necessary destroy any organic material at this point by ignition at 500° to 550° C. Acidify the cooled residue (ignited or not) with 2.5 ml 1 + 11  $\text{HCl}$  and triturate with a rubber policeman to dissolve. Centrifuge if need be to obtain a clear solution. Pipet 2.00 ml clear concentrate

<sup>2</sup> Hatcher J. T. and Wilcox L. V. Anal. Chem. 22, 567 1950

into a small flask or 30-ml. test tube. Subject a reagent blank to the same steps as the sample.

**Color Development.**—Prepare a series of B standard solutions (0.100, 0.250, 0.500, 0.750, and 1.00 mg.) in 100-ml. volume with distilled water. Pipet 2.00 ml. of each standard solution into a small flask or 30-ml. test tube.

Treat the blank and calibration standards exactly as the sample throughout the procedure. Add 2 drops concentrated HCl, then carefully introduce 10.0 ml. concentrated  $\text{H}_2\text{SO}_4$ , mix, and allow to cool to room temperature. Add 10.0 ml. carmine reagent, mix well, and after 45 to 60 min., measure the absorbance at  $585\text{ m}\mu$  in a cell of 1-cm. length or longer, using the blank as the reference.

$$B, \text{ milligrams per liter} = \frac{\text{milligrams of B} \times 1000}{\text{milliliters of sample}}.$$

### CADMIUM <sup>2,10</sup>

Nominal amounts of most ions can be tolerated in the following dithizone method. Zinc concentrations in excess of a 500 to 1 ratio of Zn to Cd cause low results. Cupric, ferric, chromate, permanganate, and other oxidizing ions oxidize dithizone in alkaline solution to diphenylthiocarbazadiazone, an interference which can be eliminated by the addition of such reductants as  $\text{NH}_2\text{OH} \cdot \text{HCl}$  or  $\text{Na}_2\text{SO}_3$ . Special steps are described for coping with interference from organic matter, Cu, Hg, Ag, Ni, and Co. The sensitivity of the method requires the thorough cleansing of all glassware with dilute  $\text{HNO}_3$ , followed by rinses with Cd-free water and dithizone solution. A wise precaution against contamination is the segregation of the glassware used for the Cd determination. As in the case of all dithizone methods, the photosensitivity of dithizone and dithizonates imposes the necessity for promptly performing the extractions out of the range of strong light. Chloroform,  $\text{CCl}_4$ , and reagents of a grade satisfactory for dithizone work should be used exclusively. A general procedure is detailed for overcoming interference from organic matter. Digestion of the sample with  $\text{HNO}_3$  and  $\text{HClO}_4$  oxidizes and volatilizes a number of ions in the original sample, thus often constituting an advantage in the determination.

Considerable caution and discretion must be exercised in the use of  $\text{HClO}_4$  for the elimination of organic interference. Perchloric acid should never be added to a hot solution containing organic matter. Fuming should be performed in hoods constructed of all stone, asbestos-cement, or both. A glass fume eradicator, of the type marketed by G. F. Smith Chemical Co., Columbus, Ohio, which connects to a water pump, may be substituted for occasional  $\text{HClO}_4$  fumings. In every case the sample should be adequately pretreated with  $\text{HNO}_3$  prior to the addition of any  $\text{HClO}_4$ .

Samples destined for extended transport to the laboratory should be preserved with concentrated  $\text{HNO}_3$  at the rate of 5 ml. per liter of sample, to prevent serious adsorption losses.

**Reagents.** Deionized Distilled Water or Redistilled Water.—These should be used for the preparation of all solutions and dilutions.

**Standard Cadmium Solution.**—(a) Dissolve 0.1000 g. pure cadmium metal in water with 5 ml. concentrated HCl, and dilute to 1000 ml. (b) Dilute 5.00 ml. stock solution, together with 2 ml. concentrated HCl, to 200 ml., to form a stand-

<sup>10</sup> Serfass, E. J., *et al.*, *Plating*, 35, 458, 1948.

ard solution containing 0.0025 mg of cadmium per 100 ml. Prepare the standard solution daily.

**Dithizone Chloroform Solution**—Dissolve 100 mg diphenylthiocarbazone (dithizone) in 100 ml  $\text{CHCl}_3$ . Stopper tightly and store in the refrigerator.

**Dithizone Carbon Tetrachloride Solution**—Dissolve 100 mg diphenylthiocarbazone in 1 liter  $\text{CCl}_4$ . Stopper tightly and store in the refrigerator. If necessary purify dithizone as follows: dissolve 100 mg dithizone in 250 ml  $\text{CCl}_4$  and pour into a 1 liter separatory funnel. Add 200 ml water and 3 ml concentrated  $\text{NH}_4\text{OH}$ . Shake well and reject the  $\text{CCl}_4$  layer. Extract with 100 ml portions  $\text{CCl}_4$  until the organic layer is clear green and reject the extracts. Transfer the purified dithizone to  $\text{CCl}_4$  by acidifying with 50 ml 1 + 1  $\text{HCl}$  and shaking vigorously with 500 ml  $\text{CCl}_4$ . Discard the aqueous layer. Draw off the dithizone  $\text{CCl}_4$  layer, wash with 100 ml water, separate and dilute with  $\text{CCl}_4$  to 1 liter.

**Potassium Sodium Tartrate Solution**—Dissolve 50 g  $\text{KNaC}_4\text{H}_4\text{O}_6 \cdot 4\text{H}_2\text{O}$  in 250 ml water. Free the solution of heavy metals by shaking with repeated 50 ml portions of dithizone  $\text{CCl}_4$  solution until the final dithizone portion shows no trace of pink. Then extract the dithizone and its yellow oxidation product with  $\text{CHCl}_3$  portions until the final organic layer remains colorless. Remove the  $\text{CHCl}_3$  with a last  $\text{CCl}_4$  extraction.

**Dimethylglyoxime Solution** 0.1 g per 100 ml 95% Ethyl Alcohol

**Nitric Acid** Concentrated

**Hydrochloric Acid** Concentrated

**Ammonium Hydroxide** Concentrated

**Perchloric Acid** 60 to 70%

**Sodium Hydroxide** 6 N

**Sodium Hydroxide** 1 N

**Chloroform**

**Carbon Tetrachloride**

**Sodium Sulfate**

**Procedure** **General Procedure for Removal of Organic Matter Interference**—Place the measured sample in an evaporating dish, casserole or beaker. Add 5 to 10 ml concentrated  $\text{HNO}_3$  and evaporate to 15 to 20 ml on a steam bath or hot plate. Cover with a watch glass when necessary to prevent losses due to spattering. If desired, place an infrared lamp over the sample to speed evaporation. Quantitatively transfer the concentrate and any residue to a 125 ml flask. Cool and add 5 ml concentrated  $\text{HNO}_3$ , 10 ml 60 to 70%  $\text{HClO}_4$  and a few glass beads. (Perform all  $\text{HClO}_4$  evaporations in a hood of stone or transient construction; alternatively, connect a glass fume ericator to a water pump for the purpose of removing the  $\text{HClO}_4$  fumes.) Evaporate carefully on a hot plate until dense  $\text{HClO}_4$  fumes just appear. Cover the flask with a watch glass and keep the solution just barely boiling until the liquid becomes clear and colorless. If necessary, add another 10 ml concentrated  $\text{HNO}_3$  to complete the oxidation. After the colorless digested solution has cooled, wash the inner walls of the flask and watch glass with sufficient water to bring the total solution volume to 50 ml. Expel the chlorine or nitrogen oxides by boiling. Remove any  $\text{SiO}_2$  residue by filtration through a sintered glass or porous filter crucible. Rinse the flask with two 5 ml portions of water and add to the filter to wash the residue. If this digestate is to serve for more than one determination, quantitatively transfer the filtrate and washings to a volumetric flask (such as 50 or 100 ml), cool, dilute to the mark and mix.

**Procedure for Cadmium.**—If necessary, first remove interfering amounts of organic matter by the steps described above.

Pipet an aliquot containing 0.0025 to 0.02 mg. Cd of the final filtrate remaining from the general procedure for removal of organic matter interference.

Prepare a blank and a series of Cd standards (0.0025-, 0.005-, 0.010-, 0.015-, and 0.020-mg.) with sufficient water to give a total volume corresponding to the sample volume or aliquot taken. Treat the blank and standards exactly as the sample throughout the procedure. In the case of a potable water free from organic matter interference and meeting USPHS drinking water standards for Cd, take a minimum sample volume of 250 ml., add 0.5 ml. concentrated HCl, and evaporate to 15 to 20 ml. If necessary, filter and wash.

If Cu, Hg, and Ag are present, add 5 ml.  $\text{KNaC}_4\text{H}_4\text{O}_6$  solution to the filtrate, and adjust with concentrated HCl or concentrated  $\text{NH}_4\text{OH}$  to pH 2.0. Quantitatively transfer to a 125-ml. separatory funnel. Extract with 5-ml. portions dithizone- $\text{CHCl}_3$  solution until the final dithizone portion remains an unchanging green color. Discard the extracts. Wash the aqueous layer with 10-ml. portions  $\text{CHCl}_3$  until the organic layer becomes colorless. Discard the washings. Wash with a 5-ml. portion  $\text{CCl}_4$ , and discard the washing.

If Ni or Co are present, quantitatively transfer the aqueous layer to a 150-ml. beaker, add 5 ml.  $\text{KNaC}_4\text{H}_4\text{O}_6$  solution, and adjust with concentrated  $\text{NH}_4\text{OH}$  to pH 8.5 to 9.0. Quantitatively return the solution to the separatory funnel, add 5 ml. dimethylglyoxime solution, and shake vigorously for 30 sec. Extract with 3 or more 10-ml. portions  $\text{CHCl}_3$  until the white precipitate of excess dimethylglyoxime has been removed. Discard the extracts. Wash the aqueous layer with one 5-ml. portion  $\text{CCl}_4$ , and discard the washing.

Make the aqueous layer in the separatory funnel strongly basic by adding 4 ml. 6 N NaOH, and mix. Follow with 5 ml. dithizone- $\text{CCl}_4$  solution and shake thoroughly. Transfer the organic layer to a clean separatory funnel. Perform a second extraction with a 5-ml. portion dithizone- $\text{CCl}_4$  solution, and thereafter with 3-ml. portions until the Cd is completely removed, as evidenced by the absence of pink or slight yellow color in the final dithizone portion. Wash the combined  $\text{CCl}_4$  extracts with two 10-ml. portions 1 N NaOH, and then with water. Discard the aqueous washings. Filter the red Cd dithizonate layer through a small filter paper, or a cotton or glass-wool plug, or a fritted-glass funnel containing a 1-g. layer of  $\text{Na}_2\text{SO}_4$  into a 25-ml. volumetric flask. Wash the filter with a little  $\text{CCl}_4$  and add the washing to the volumetric flask. Dilute to the mark with  $\text{CCl}_4$ , mix well, and rapidly determine the absorbance at 515  $m\mu$  against a reference of pure  $\text{CCl}_4$  or the reagent blank. If pure  $\text{CCl}_4$  is used as the reference, correct the sample result by deducting the Cd content of the reagent blank carried through the entire procedure.

$$\text{Cd, milligrams per liter} = \frac{A \times 1000}{\text{milliliters of sample}} \times \frac{B}{C}$$

where  $A$  = milligrams of Cd found photometrically or visually. The ratio  $B/C$  applies only when a large sample is digested for removal of organic matter interference, the volume then made up to  $B$ , and an aliquot,  $C$ , taken from it for color development.

## CALCIUM

The classical gravimetric and titrimetric oxalate methods for Ca are recognized to yield the most reliable results. Generally a single precipitation of  $\text{CaC}_2\text{O}_4$  is adequate. Recourse to reprecipitation is taken only for the most exact work. The relative simplicity of the EDTA complexometric method commends itself for routine control operations.

OXALATE METHODS<sup>2</sup>

Silica, Al, Fe, Mn,  $\text{PO}_4$ , and suspended matter must be removed before the Ca is precipitated as  $\text{CaC}_2\text{O}_4$ . Since  $(\text{NH}_4)_2\text{C}_2\text{O}_4$  reagent also precipitates Sr, a flame photometric determination for Sr should be conducted so that the proper deduction can be applied to the Ca result.

**Reagents** Ammonium Oxalate Solution 10 g  $(\text{NH}_4)_2\text{C}_2\text{O}_4 \cdot \text{H}_2\text{O}$  per 250 ml

Ammonium Chloride Wash Solution 20 g per liter

Hydrochloric Acid Concentrated

Hydrochloric Acid 1 + 1

Methyl Red Indicator

Ammonium Hydroxide 3 N

Ammonium Hydroxide 1 + 99

Ammonium Persulfate

Ferric Chloride

**Standard Potassium Permanganate Titrant** 0.05 N—Filter the supernatant from an aged solution of 0.1 N  $\text{KMnO}_4$  through a fritted glass crucible and dilute with an equal volume of distilled water. Standardize daily against accurately weighed 100 to 200 mg portions of  $\text{Na}_2\text{C}_2\text{O}_4$ , primary standard grade (dried at 105°C). Place the  $\text{Na}_2\text{C}_2\text{O}_4$  in a beaker, add 10 ml 1 + 1  $\text{H}_2\text{SO}_4$  and 100 ml distilled water, and titrate the heated solution to the typical pink end point used for the sample.

$$\text{Normality of } \text{KMnO}_4 = \frac{\text{milligrams of } \text{Na}_2\text{C}_2\text{O}_4}{(A - B) \times 6.701}$$

where  $A$  = milliliters of titration for  $\text{Na}_2\text{C}_2\text{O}_4$  and

$B$  = milliliters of titration for blank. The equivalence of 0.0500 N  $\text{KMnO}_4$  is 1.002 mg Ca per 1.00 ml.

Sulfuric Acid 1 + 1

**Procedure** Removal of Interference—Remove the  $\text{SiO}_2$  and suspended matter as described in Gravimetric Method under Silica below p. 2475.

Next remove  $\text{PO}_4$  interference by adding sufficient  $\text{FeCl}_3$  to yield a red brown precipitate in the filtrate from the gravimetric determination for  $\text{SiO}_2$ .<sup>11</sup>

Then remove Al, Fe, and Mn interference by concentrating the filtrate from the gravimetric determination for  $\text{SiO}_2$  to 120 to 150 ml. If necessary, bring the total volume of concentrated HCl in the  $\text{SiO}_2$  filtrate to 10 ml at this point with the addition of more concentrated HCl. Add with mixing several drops methyl red indicator, enough 3 N  $\text{NH}_4\text{OH}$  to change the indicator color to yellow, and 1 g  $(\text{NH}_4)_2\text{S}_2\text{O}_8$ . After the solution begins to boil, resume the careful addition of 3 N  $\text{NH}_4\text{OH}$  until the solution tests slightly alkaline to litmus paper and the steam yields a distinct but not a strong odor of  $\text{NH}_3$ . Allow the hot solution to

<sup>11</sup> Manual on Industrial Water and Industrial Waste Water, 2nd Ed., ASTM, Philadelphia, 1959.

stand exactly 10 min. after 1 to 2 min. of boiling. Wash the filtered precipitate 3 to 4 times with  $\text{NH}_4\text{Cl}$  solution. Dilute or concentrate the filtrate and washings to a convenient volume.

**Precipitation of Calcium.**—Select a sample volume containing less than 250 mg. Ca for a gravimetric finish, and less than 50 mg. for a titrimetric finish. If need be, dilute to 200 ml. Alternatively, concentrate the filtrate from the interference removal operations to 200 ml. Add several drops methyl red indicator and enough 1 + 1 HCl to change the indicator color to pink. After 1 min. of boiling, add 50 ml.  $(\text{NH}_4)_2\text{C}_2\text{O}_4$  solution. Redissolve any precipitate that may form at this point with a minimum of 1 + 1 HCl. To the warm, but not boiling, solution, add with constant stirring 5 ml. 3 N  $\text{NH}_4\text{OH}$  drop by drop from a buret. After the covered mixture has digested at 90°C. for 90 min., add slowly over a period of several minutes more 3 N  $\text{NH}_4\text{OH}$  until the yellow indicator color returns (to check on thoroughness of precipitation). Digest another 15 min. at 90°C. If a single precipitation is adequate, complete the determination gravimetrically or titrimetrically. Otherwise, perform the Ca reprecipitation as follows.

**Reprecipitation of Calcium.**—Remove the precipitate with an ashless, fine-textured, retentive filter paper, and wash 3 to 4 times with cold 1 + 99  $\text{NH}_4\text{OH}$ , or until the washings become free from Cl. If desired, retain the filtrate and washings for the gravimetric determination of Mg. Dissolve the precipitate by pouring onto the filter 10 ml. 1 + 1 HCl in small portions, and then washing the filter paper with 3 to 4 small portions of hot, distilled water. Collect the filtrate in the original beaker, dilute to 175 ml.; and reprecipitate and digest the Ca as previously described.

**Gravimetric Finish.**—Remove the precipitate with an ashless, fine-textured, retentive filter paper, and wash 3 to 4 times with cold 1 + 99  $\text{NH}_4\text{OH}$ , or until free from Cl. If desired, retain the filtrate and washings for the gravimetric determination of Mg. Carefully char the filter paper in a crucible that has previously been ignited and weighed. Burn off the final traces of paper without causing a flame, and ignite to CaO at 1100° to 1200°C. for 30 to 60 min., or to constant weight. Cool the crucible in an efficient desiccator and weigh.

$$\text{Ca, milligrams per liter} = \frac{\text{milligrams of CaO} \times 714.7}{\text{milliliters of sample}}$$

**Titrimetric Finish.**—Decant the supernatant through a filter crucible. Wash the beaker and precipitate with at least four 5- to 10-ml. portions 1 + 99  $\text{NH}_4\text{OH}$  to remove all soluble oxalate. If desired, reserve the filtrate and washings for the gravimetric determination of Mg. Return the crucible in a horizontal position to the original beaker and cover with distilled water. Add 10 ml. 1 + 1  $\text{H}_2\text{SO}_4$ , stirring the interior of the crucible to dissolve all the  $\text{CaC}_2\text{O}_4$ . Heat nearly to boiling, and titrate with standard 0.05 N  $\text{KMnO}_4$  to a faint pink end point. Determine the titration blank on 10 ml. 1 + 1  $\text{H}_2\text{SO}_4$  and the same volume of distilled water as was used for the sample.

$$\text{Ca, milligrams per liter} = \frac{(A - B) \times N \times 20040}{\text{milliliters of sample}}$$

where  $A$  = milliliters of titration for sample,  
 $B$  = milliliters of titration for blank, and  
 $N$  = normality of  $\text{KMnO}_4$ .

COMPLEXOMETRIC METHOD<sup>2 11 12 13 14 15</sup>

The following individual interferences in the specified concentrations can be tolerated in the described procedure 20 mg per liter for ferrous or ferric ions 10 mg per liter for manganous ion 5 mg per liter for Al or Pb or Sn or Zn and 2 mg per liter for Cu Orthophosphate precipitates Ca at pH 12 to 13 while alkalinity in excess of 30 mg per liter may cause an indistinct end point with hard waters In the presence of murexide Sr titrates sluggishly like Ca whereas Ba affects the titration adversely by giving a poor end point or no end point The titration should be completed within 5 min to prevent  $\text{CaCO}_3$  precipitation at a pH of 12 to 13 In addition to ammonium purpurate Calcon (Eriochrome Blue Black R) and Calcein (fluorescein methyleneiminodiacetic acid) can be used for the complexometric titration of Ca

**Reagents** Standard EDTA Titrant 0.01 M (0.02 N) —Preparation and standardization described in Hardness p 2434 below

**Indicator**—Either a solid (a) or liquid (b) formulation is satisfactory (a) 0.2 g ammonium purpurate (murexide) + 100 g NaCl ground together in a mortar This indicator yields a color change from salmon to orchid purple (b) 0.15 g ammonium purpurate (murexide)/100 g absolute ethylene glycol

Sodium Hydroxide, 1 N

Hydrochloric Acid 0.02 N

**Procedure**—Prepare a color comparison blank in a white porcelain casserole by stirring 20 ml 1 N NaOH 0.2 g solid indicator mixture (or 4 to 6 drops indicator solution) into 50 ml distilled water and sufficient standard EDTA titrant (0.05 to 0.10 ml) to produce an unchanging purple color Pipet into a similar white porcelain casserole a 50 ml sample or dilute to 50 ml an aliquot containing 5 to 10 mg Ca Neutralize the alkalinity with 0.02 N HCl boil 2 to 3 min to expel the  $\text{CO}_2$  and cool to room temperature Add 20 ml 1 N NaOH or a volume sufficient to produce a pH of 12 to 13 and mix Add 0.2 g powdered indicator mixture or 4 to 6 drops indicator solution and mix Stirring constantly titrate with standard 0.01 M EDTA to the color of the comparison blank Check the end point by adding 1 or 2 drops of titrant in excess to be sure that no further deepening of the purple color takes place

$$\text{Ca, milligrams per liter} = \frac{(A - B) \times C \times 400.4}{\text{milliliters of sample}}$$

where  $A$  = milliliters of titration for sample,

$B$  = 0.10 ml titration for blank, and

$C$  = milligrams of  $\text{CaCO}_3$  equivalent of 1.00 ml of EDTA titrant

<sup>12</sup> Betz J. D. and Noll C. A. J. Am. Water Works Assn. 42, 749 1950

<sup>13</sup> Goetz C. A. and Smith R. G. Iowa State J. Science 34, 101 1959

<sup>14</sup> Schwarzenbach G. Biederman W. and Bangerter B. Helv. Chim. Acta 29 811 1946

<sup>15</sup> Two United States patents (Nos. 2583890 and 2583891) have been issued to G. Schwarzenbach anent complexometric methods in water analysis Nothing contained in this volume is to be construed as granting any right by implication or otherwise for the use of these methods nor as insuring anyone against liability for infringement of these patents



CARBON DIOXIDE <sup>2, 16, 17</sup>

The CO<sub>2</sub> content often is the sole contributor to the acidity of the potable natural water sample. On this account, the CO<sub>2</sub> determination bears a close resemblance to the acidity titration. The differences reside in the concentrations of the titrants and the fact that the titration is conducted in a manner that minimizes the escape of the volatile CO<sub>2</sub> gas. Either Na<sub>2</sub>CO<sub>3</sub> or NaOH are acceptable titrants. At best this method affords only an estimate of the CO<sub>2</sub> content when a field determination becomes impossible. The presence of acid mine wastes invalidates the CO<sub>2</sub> results.

**Reagents.** Boiled Distilled Water.—This should be used in the preparation of all solutions.

**Standard Sodium Hydroxide Titrant, 0.0227 N.**—Dilute 22.7 ml. 1 N NaOH to 1 liter with water. Standardize as described under "Acidity," above, p. 2398. The equivalence of 0.0227 N NaOH is 1.00 mg. CO<sub>2</sub> per 1.00 ml.

**Standard Sodium Carbonate Solution, 0.0454 N.**—Dissolve 2.407 g. Na<sub>2</sub>CO<sub>3</sub>, primary standard grade (dried at 140°C.), and dilute to 1000 ml. with water. Prepare daily or protect from atmospheric CO<sub>2</sub> with a soda lime tube. The equivalence of 0.0454 N Na<sub>2</sub>CO<sub>3</sub> is 1.00 mg. CO<sub>2</sub> per 1.00 ml.

Sodium Bicarbonate pH 8.3 Color Standard.

Phenolphthalein Indicator.

**Procedure.** Field Determination.—Attach a rubber tube to the water tap, and place the open end of the tube at the bottom of a 100-ml., graduated cylinder or Nessler tube. Let the water overflow the cylinder to the extent of 2 or 3 times the cylinder volume, and then withdraw the tube as the water continues to run. Quickly adjust the water volume in the cylinder to the 100-ml. mark, and add 0.25 to 0.5 ml. (5 to 10 drops) phenolphthalein indicator. If the sample remains colorless, titrate rapidly with standard 0.0227 N NaOH or standard 0.0454 N Na<sub>2</sub>CO<sub>3</sub> to the color of the pH 8.3 NaHCO<sub>3</sub> color standard resting alongside in an identical graduated cylinder or Nessler tube. Mix the titrant and the sample gently with a stirring rod. Repeat the determination on a second sample by adding the full alkaline volume of the first titration, and, if the sample remains colorless, complete the titration in the prescribed manner. Accept the second titration as the more reliable result.

**Laboratory Determination.**—Extend the rubber sampling tube to the bottom of a borosilicate-glass bottle, and allow the water to overflow to the extent of 2 or 3 times the bottle capacity. Replace the glass stopper so as to entrain no air. Refrigerate the sample during transport to the laboratory and until ready for testing. Siphon the sample into a 100-ml. graduated cylinder or Nessler tube, and allow some overflow to take place. Complete the determination as described for the field determination.

When the titrant is NaOH,

$$\text{CO}_2, \text{ milligrams per liter} = \frac{A \times N \times 44000}{\text{milliliters of sample}}$$

<sup>16</sup> Am. Public Health Assn., and Am. Water Works Assn., Standard Methods for the Examination of Water and Sewage, 9th Ed., New York, 1946.

<sup>17</sup> Approved Methods for the Physical and Chemical Examination of Water, 3rd Ed., Institution of Water Engineers, Parliament Mansions, Abbey Orchard St., London, S.W.1, 1960.

When the titrant is  $\text{Na}_2\text{CO}_3$ ,

$$\text{CO}_2, \text{ milligrams per liter} = \frac{A \times N \times 22000}{\text{milliliters of sample}}$$

where  $A$  = milliliters of titration for sample, and

$N$  = normality of titrant

### CHLORIDE <sup>2 11</sup>

Bromide and iodide react quantitatively with  $\text{AgNO}_3$ , and must be absent or compensated for in the sample. Orthophosphate in excess of 25 mg per liter precipitates  $\text{Ag}_3\text{PO}_4$ , while Fe in excess of 10 mg per liter masks the titration end point.

Both inorganic and organic sulfur reductants may interfere with the titration.<sup>11</sup> The formation of a black  $\text{Ag}_2\text{S}$  precipitate with inorganic sulfide obscures the end point, and leads to an incomplete titration. Low readings are also caused by thiourea (0.4 mg per liter of S), thioacetic acid (0.1 mg per liter of S), and methyl disulfide (8 mg per liter of S). On the other hand, such organic sulfur compounds as the mercaptans (10 mg per liter of S) and alkyl and aryl sulfides (25 mg per liter of S) give high results. Evaporating the sample to dryness on a steam or water bath, rubbing the residue with 0.5 ml 30%  $\text{H}_2\text{O}_2$ , and redissolving the residue with 50 or 100 ml distilled water can eliminate much of this interference. Hydrogen peroxide also oxidizes sulfite in neutral solution and thiosulfate in alkaline solution. Acidification of the sample and boiling can eliminate cyanide and inorganic sulfide.

**Reagents.** Deionized Distilled Water or Redistilled Water.—These should be used for the preparation of all solutions and dilutions.

**Standard Silver Nitrate Titrant, 0.0141  $N$ .**—Dissolve 2.896 g  $\text{AgNO}_3$ , and dilute to 1000 ml with water. Standardize against 0.0141  $N$   $\text{NaCl}$  under exactly the same conditions (similar volumes of final solution and  $\text{K}_2\text{CrO}_4$  indicator) that the water samples are titrated under. Pipet a volume of standard  $\text{NaCl}$  that approximates either the average or median (whichever is applicable) Cl usually prevailing in the water samples determined in the particular laboratory. The equivalence of 0.0141  $N$   $\text{AgNO}_3$  is 0.500 mg Cl per 100 ml. Store in a brown bottle or in the dark.

**Standard Sodium Chloride Solution, 0.0141  $N$ .**—Dissolve 0.8241 g.  $\text{NaCl}$  dried at  $140^\circ\text{C}$ , and dilute to 1000 ml with water. The Cl equivalence of this solution is 0.500 mg per 100 ml.

**Potassium Chromate Indicator.**—Dissolve 50 g  $\text{K}_2\text{CrO}_4$  in 1 liter of water, add sufficient  $\text{AgNO}_3$  solution to produce a slight red precipitate, and filter after the suspension has remained in the dark for 24 hr.

**Phenolphthalein Indicator.**

**Hydrogen Peroxide, 30%**

**Calcium Carbonate.**

**Sodium Hydroxide, 1  $N$ .**

**Sulfuric Acid, 1  $N$ .**

**Nitric Acid, 1  $N$ .**

**Aluminum Hydroxide, Suspension.**

<sup>11</sup> Taras, M. J., *Water and Sewage Works*, 102, 412, 1955.

**Procedure. Sample Pretreatment.**—When an interfering amount of color is present, apply 3 ml. well-shaken  $\text{Al}(\text{OH})_3$  suspension to each 100 ml. sample, stir, and allow the floc to settle several times. Then filter and wash the floc. Collect and combine the filtrate and washings.

Remove sulfite by adding 1 ml. 30%  $\text{H}_2\text{O}_2$  to each 100 ml. sample adjusted to a neutral pH.

Remove thiosulfate by making the sample alkaline to phenolphthalein indicator with 1 *N* NaOH. Add 1 ml. 30%  $\text{H}_2\text{O}_2$ , stir, and after 5 min., neutralize with 1 *N*  $\text{H}_2\text{SO}_4$ .

Expel cyanide and sulfide by acidifying the sample with 1 *N*  $\text{H}_2\text{SO}_4$  to pH 4, boiling, and neutralizing the sample with 1 *N* NaOH or a small amount of solid  $\text{CaCO}_3$ .

Neutralize with 1 *N* NaOH or a small amount of solid  $\text{CaCO}_3$  a sample whose pH is less than 7.

Neutralize with 1 *N*  $\text{H}_2\text{SO}_4$  or  $\text{HNO}_3$  a sample whose pH exceeds 10.

**Titration.**—Prepare a color comparison blank in a white porcelain casserole by stirring 1.0 ml.  $\text{K}_2\text{CrO}_4$  indicator and 0.20 ml. standard 0.0141 *N*  $\text{AgNO}_3$  into 100 ml. deionized distilled water or redistilled water. Pipet into a similar white porcelain casserole 100 ml. sample; or dilute an aliquot so that no more than 10 mg. Cl is contained in 100 ml. Add 1.0 ml.  $\text{K}_2\text{CrO}_4$  indicator and, stirring constantly, titrate with standard 0.0141 *N*  $\text{AgNO}_3$  to the color of the comparison blank.

$$\text{Cl, milligrams per liter} = \frac{(A - B) \times N \times 35460}{\text{milliliters of sample}}$$

where *A* = milliliters of titration for sample,

*B* = 0.20 ml. of titration for blank, and

*N* = normality of  $\text{AgNO}_3$ .

## RESIDUAL CHLORINE

**Applicability of Residual Chlorine Methods.**—The iodometric method finds greatest use for the determination of high chlorine concentrations above 1 mg. per liter and in the standardization of chlorine dosing water. The orthotolidine-arsenite (OTA) colorimetric method is widely employed in water treatment plants for the routine control of the chlorination process. The amperometric method is largely free of interference from color and turbidity, which may affect the colors of the *o*-tolidine and iodometric methods. The method is suitable for the determination of residual chlorine concentrations up to 5 mg. per liter, and is capable of differentiating the 3 principal chlorine fractions generally prevalent in water.

The impossibility of preserving the residual chlorine of a water sample underscores the importance of performing the determination as soon after collection as possible.

## IODOMETRIC METHOD<sup>2</sup>

The iodometric titration of total available chlorine is performed in an acid medium. Sulfuric acid may be substituted for the specified acetic acid when interferences are known to be absent. Conducting the titration at a neutral pH minimizes interference from nitrite, manganic, and ferric ions.

TABLE 48-5 PERMANENT COLOR STANDARDS EQUIVALENT TO 10 TO 10 MG PER LITER OF CHLORINE

Chlorine Equivalent, mg per l	Milliliters of Stock Chromate Dichromate Solution for Cell Depth of			
	2.5 to 5 cm	10 cm	20 cm	24 to 30 cm
1	10.0	10.0	10.0	10.0
1.5	15.0	15.0	15.0	15.0
2	19.5	19.5	19.7	20.0
3	27.0	27.5	29.0	30.0
4	34.5	35.0	39.0	40.0
5	42.0	43.0	48.0	50.0
6	49.0	51.0	58.0	60.0
7	56.5	59.0	68.0	70.0
8	64.0	67.0	77.5	80.0
9	72.0	75.5	87.0	90.0
10	80.0	84.0	97.0	100.0

**Decolorizing Solution**—Mercaptosuccinic acid is the most satisfactory decolorizer but minimal quantities of 0.1 *N*  $\text{Na}_2\text{S}_2\text{O}_3$  or  $\text{Na}_2\text{SO}_3$  may be used alternatively provided the latter 2 solutions produce no interfering sulfur colloid or precipitate with the treated water sample.

**Mercaptosuccinic Acid (Also Called Thiomalic Acid) Solution** 10 g per 100 ml  
**Sodium Sulfite Solution**, 10 g per 100 ml

**Chlorine Demand Free Water**—Treat a distilled water free of  $\text{NH}_3$  or nitrite with sufficient standard chlorine solution (preparation described under Chlorine Demand below) to produce a free available chlorine residual of 2 to 5 mg per liter. Allow the water to stand overnight or longer then remove the residual chlorine by exposure to direct sunlight or ultraviolet irradiation. Store in a tightly stoppered bottle to protect from contaminating fumes.

**Procedure Free Available Residual Chlorine**—Use 0.5 ml o-tolidine reagent and 0.5 ml  $\text{NaAsO}_2$  solution for each 95 ml sample taken in the procedure. Rapidly chill the sample to 15°C and preferably less. Place the proper volume of o-tolidine reagent in the tube or bottle and add a measured volume of water sample. Mix quickly and thoroughly and within 5 to 10 sec add the proper volume of  $\text{NaAsO}_2$  solution. Mix again and promptly compare the color against permanent color standards. Record as reading *A*.

**Total Available Residual Chlorine**—Use 0.5 ml o-tolidine reagent for each 95 ml sample taken. Place the proper volume of o-tolidine reagent in the tube or bottle and add a measured volume of water sample. Mix thoroughly and compare the maximum color developed normally within 5 min against permanent color standards. Record as reading *C*.

**Color and Turbidity Blank**—(a) Use the same volumes of  $\text{NaAsO}_2$  solution, o-tolidine reagent and sample as in the free available and total available residual chlorine determinations. Place the proper volume of  $\text{NaAsO}_2$  solution in the tube or bottle and add the proper volume of sample. Mix promptly and thor

oughly, then add the proper volume of *o*-tolidine reagent. Mix again, and immediately compare the color against permanent color standards. Record reading as blank 1. Compare the same blank against permanent color standards 5 min. later, and record as blank 2. (b) Instead of preparing a separate color and turbidity blank as in step (a), add 1 to 2 drops of decolorizing solution (preferably mercaptosuccinic acid, or 0.1 *N* Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>, or Na<sub>2</sub>SO<sub>3</sub> solution), to the yellow chlorine-orthotolidine color developed in the free available residual chlorine procedure or the total available residual chlorine procedure. Mix promptly and thoroughly until the yellow *o*-tolidine color disappears within 1 min., and again compare with the permanent color standards. (c) If necessary, remove excessive turbidity by briefly centrifuging the sample to improve the visual comparison or to bring the sample within nulling range of the photometer.

**Photometric Measurement.**—Measure the color developed in the free available residual chlorine and the total available residual chlorine procedures in a photometer. Use a light path of 5 cm. and a wavelength range of 400 to 450  $m\mu$  for residual chlorine concentrations of 0.02 to 0.3 mg. per liter; a light path of 1 cm. and a wavelength range of 400 to 450  $m\mu$  for residual chlorine concentrations of 0.1 to 1.5 mg. per liter; and a light path of 1 cm. and a wavelength of 490  $m\mu$  for residual chlorine concentrations of 0.5 to 7.0 mg. per liter. Prepare a calibration curve by subjecting known residual chlorine concentrations in chlorine demand-free water to exactly the same steps used in the treatment of the water samples.

Free available residual chlorine = reading *A* — blank 1.

Combined available residual chlorine = reading *C* — reading *A*.

Total available residual chlorine = reading *C* — blank 2.

**Drop Dilution Modification.**—Adopt the following modification for the approximate estimation of residual chlorine concentrations above 10 mg. per liter, such as are applied in the disinfection of water mains or tanks. Use 0.5 ml. *o*-tolidine reagent for each 9.5 ml. distilled water taken for dilution. Place the proper volume of *o*-tolidine reagent in the tube or bottle, add a measured volume of distilled water, and mix thoroughly. Add 1 drop (0.05 ml.) test sample, mix thoroughly, and immediately estimate the resulting yellow color in a suitable comparison device. Continue this procedure with an increasing number of drops of test sample until a yellow color is obtained in the diluted portion corresponding to at least 0.1 mg. per liter in the matching chlorine standard.

$$\text{Free available residual chlorine, milligrams per liter} = \frac{D \times E \times 20}{F}$$

where *D* = milliliters of volume of tube, cell, or bottle

*E* = milligrams per liter value of chlorine standard matching color of diluted sample

*F* = number of drops of test sample.

#### AMPEROMETRIC METHOD <sup>22</sup>, <sup>11</sup>, <sup>22</sup>

The amperometric method affords an estimate of the residual chlorine fractions. The pH must be adjusted to 7 for the determination of the free available chlorine and some of the NCl<sub>3</sub> and ClO<sub>2</sub>. Free halogens other than chlorine, together with

<sup>22</sup> Marks, H. C., Williams, D. B., and Glasgow, G. U., J. Am. Water Works Assn., 43, 201, 1951.

bromide and iodide may also contribute spuriously high readings at this point. The addition of a small amount of KI at pH 7 yields an estimate of the  $\text{NH}_4\text{Cl}$  fraction. Lowering the pH to 4.0 enables an estimate of the  $\text{NH}_4\text{Cl}_2$  and some of the  $\text{NCl}_3$  in the presence of KI. Organic chloramines may titrate in the  $\text{NH}_4\text{Cl}$  or  $\text{NCl}_2$  fraction. Cupric ions may cause erratic behavior while cuprous and Ag ions may poison the electrode. The titration period should be prolonged at low temperatures because of the slow electrode response. A pH above 7.5 also slows the reaction rate which accounts for the use of the pH 7 phosphate buffer in the procedure. Standard 0.00564 N  $\text{Na}_2\text{S}_2\text{O}_3$  may be substituted for phenyl arsenoxide in the amperometric titration of total residual chlorine alone where differentiation of the  $\text{NH}_4\text{Cl}$  and  $\text{NH}_4\text{Cl}_2$  fractions is unneeded.

**Apparatus**—The components of the amperometric titrator are illustrated in the schematic diagram in Fig. 48.4. The cell unit consists of a noble metal electrode and a reference electrode of silver-silver chloride in a saturated NaCl solution connected into the circuit by means of a salt bridge without diffusion of electrolyte. A microammeter, an electrically operated agitator and a 1 ml buret graduated in units of 0.01 ml complete the essential elements of the amperometric titrator. The agitator and all glassware must be thoroughly cleansed of chlorine consuming contaminants then immersed in 1 to 10 mg per liter free available chlorine and finally rinsed with chlorine demand free water.

**Reagents** **Standard Phenylarsenoxide Titrant 0.00564 N**—Dissolve 0.8 g phenylarsenoxide (a product of Wallace & Tiernan Inc. Belleville N. J.) in 150 ml distilled water containing 1.8 g NaOH allow the insoluble matter to settle and decant 110 ml of the supernatant liquid into 800 ml distilled water. Adjust the solution to a pH of 6 to 7 with 1 + 1 HCl and dilute to 1 liter. Standardize the solution to 0.00564 N against 0.0282 N iodine solution using the amperometric titrator for the normality determinations. Preserve with 1 ml  $\text{CHCl}_3$ . The equivalence of 0.00564 N  $\text{C}_6\text{H}_5\text{AsO}$  is 0.200 mg available chlorine per 1.00 ml.

**Standard Sodium Arsenite Solution 0.1000 N**—Dissolve 4.946 g  $\text{As}_2\text{O}_3$  primary standard grade (dried at 105°C) in 40 ml distilled water containing 10 g NaOH by heating the solution to about 35°C and stirring until the solution is clear and free of floating material. Dilute to 250 ml, convert all the NaOH to  $\text{NaHCO}_3$  by saturating the solution with  $\text{CO}_2$  and make up to 1000 ml.

**Stock Iodine Solution 0.1 N**—Dissolve 40 g KI in 50 ml distilled water and add 12.7 g resublimed iodine with stirring. When solution is complete dilute to 1 liter and store in a dark bottle.

**Standard Iodine Solution 0.0282 N**—Place 2.5 g KI in a 1 liter volumetric flask and dissolve in a little distilled water. Add the calculated volume of 0.1 N iodine solution and dilute to the mark. Store in a cool dark place. Standardize daily as follows: pipet 5 or 10 ml standard 0.1000 N sodium arsenite into a flask, add 50 ml distilled water and 1 to 2 ml starch indicator and titrate with 0.0282 N iodine to the first appearance of a persistent blue color. For accurate results saturate the solution with  $\text{CO}_2$  just before the blue end point is reached.

**Phosphate Buffer Solution pH 7**—Dissolve 25.4 g  $\text{KH}_2\text{PO}_4$  and 34.1 g  $\text{Na}_2\text{HPO}_4$  in 900 ml distilled water and destroy the ammonium contamination by chlorinating with 20 to 30 mg available chlorine in the form of  $\text{NaOCl}$  solution. After standing overnight in the dark dechlorinate by ultraviolet irradiation from a lamp or exposure to sunlight or by very careful addition of dilute  $\text{Na}_2\text{SO}_3$  solution.

**Acetate Buffer Solution, pH 4**—Dissolve 243 g  $\text{NaC}_2\text{H}_3\text{O}_2 \cdot 3\text{H}_2\text{O}$  and 480 g (455 ml) glacial acetic acid and dilute to 1 liter with distilled water.

Potassium Iodide Solution, 50 g. per liter.

**Procedure.**—Select a sample volume that will require less than 2 ml. 0.00564 *N* phenylarsenoxide titrant. For a residual chlorine concentration up to 2 mg. per liter, take a 200-ml. sample, and a 100-ml. sample for higher residuals.

**Free Available Residual Chlorine.**—Add 1 ml. phosphate buffer solution, immerse the electrode in the sample, start the stirrer, and add standard 0.00564 *N* phenyl-

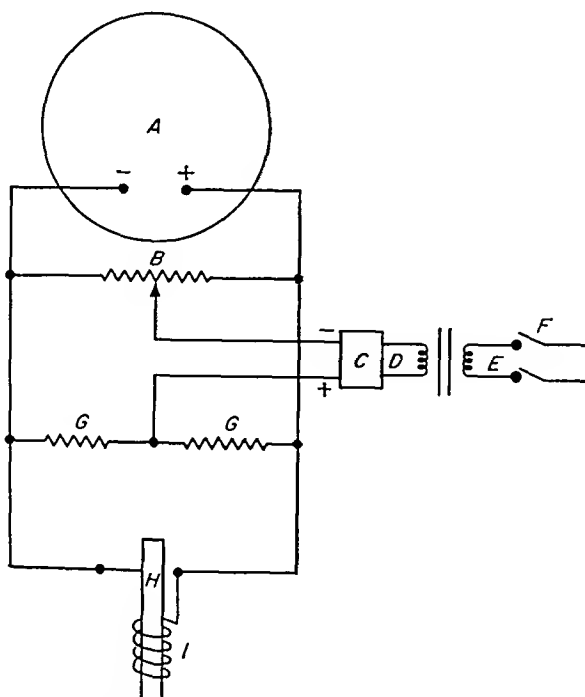


FIG. 48-4. Circuit Diagram of Amperometric Titrator: *A*, Microammeter; *B*, Zero Adjusting Potentiometer; *C*, Rectifier; *D*, Wire Wrapped Around Motor Field; *E*, Stirring Motor Field; *F*, Switch; *G*, Resistor; *H*, Silver Electrode; *I*, Platinum Electrode. (Reproduced with permission from Manual on Industrial Water and Industrial Wastewater, 2nd Ed., ASTM, Philadelphia, 1959.)

arsenoxide dropwise from the buret until the galvanometer pointer ceases to move. Wait a few seconds between successive titrant additions to allow completion of the reaction. Record as buret reading *A*.

**Monochloramine.**—Add 0.2 ml. KI solution and continue titrating with standard 0.00564 *N* phenylarsenoxide to the cessation of pointer movement. Record as buret reading *B*.

**Dichloramine.**—Add 1 ml. acetate buffer solution and 1 ml. KI solution, and complete the titration with standard 0.00564 *N* phenylarsenoxide to the cessation of pointer movement. Record as buret reading *C*.

Free available residual chlorine titration = reading *A*.

Available  $\text{NH}_2\text{Cl}$  titration = reading *B* — reading *A*.

Available  $\text{NHCl}_2$  titration = reading *C* — reading *B*.

Substitute the net titration values in the following equation to obtain the concentration of each chlorine fraction.

$$\text{Available chlorine, milligrams per liter} = \frac{D \times 200}{\text{milliliters of sample}}$$

where  $D$  = free available residual chlorine titration, or available  $\text{NH}_2\text{Cl}$  titration, or available  $\text{NHCl}_2$  titration

When the free available residual and the combined available residual chlorine alone are desired, proceed directly from reading  $A$  to reading  $C$

### CHLORINE DEMAND <sup>2</sup>

All such experimental conditions as temperature, contact time, and chlorine dosage significantly affect the chlorine demand (also called chlorine requirement) of a water. The chlorine demand determination is usually performed for the purpose of obtaining data that can be related to water plant treatment. The motive may be the improvement of bacteriological, chemical, physical, or taste and odor qualities of the water. For this reason the test conditions are subject to considerable variation and are tied directly to the objective at hand. A laboratory and a field modification applicable to many situations are described below. Every precaution should be taken to conduct the determination away from the presence of direct sunlight. If the investigation has a bacteriological objective, all glassware should be thoroughly cleaned and sterilized.

**Reagents** Standard Chlorine Solution for Laboratory Determination—Carefully pass gaseous chlorine into distilled or tap water until the solution contains 0.1 to 1.0 mg per milliliter of available chlorine. Prepare a chlorine solution of such strength that the volume of the dosed samples will be increased less than 5%. Store in a glass stoppered, brown bottle. Standardize the chlorine solution immediately before use by dissolving 1 g  $\text{KI}$  in 25 ml distilled water containing 2 ml glacial acetic acid or 1 ml concentrated  $\text{H}_2\text{SO}_4$ , adding 25.00 or 50.00 ml chlorine solution, and titrating with standard 0.0250  $N$   $\text{Na}_2\text{S}_2\text{O}_8$  titrant (prepare as described under 'Dissolved Oxygen, below p 2457) to the first disappearance of the blue starch indicator color.

$$\text{Chlorine milligrams per milliliter} = \frac{A \times V \times 35.46}{\text{milliliters of chlorine solution}}$$

where  $A$  = milliliters of  $\text{Na}_2\text{S}_2\text{O}_8$  titrant used,

$N$  = normality of  $\text{Na}_2\text{S}_2\text{O}_8$

**Standard Chlorine Solution for Field Determination**—Dilute 1 volume of 5% household bleaching solution with 4 volumes of distilled water. Standardize as described in the preceding paragraph, but measure out 20 drops of chlorine solution for titration with the same medicine dropper destined for field use. Adjust the chlorine solution to a concentration of 10 mg. per milliliter or 0.5 mg per drop, which upon addition to a 500 ml sample represents a chlorine dosage of 1 mg per liter.

**All Reagents Required for Residual Chlorine Determination.**

**Procedure** Laboratory Determination—Measure a 500 ml sample into each of 10 brown, glass stoppered bottles or flasks, and bring to the desired temperature. Mixing all the while, add to the first sample bottle an amount of standard chlorine



solution that will leave no residual chlorine at the end of the desired contact period. Increase in regular steps the amount of chlorine applied to the succeeding sample bottles in the series. Use steps of 0.1 mg. per liter chlorine for a water sample of low chlorine demand, and 1.0 mg. per liter increments for a water exerting a high chlorine demand. Allow the treated samples to stand for the required time in the dark at the desired temperature. Determine the residual chlorine by the orthotolidine-arsenite, iodometric, or amperometric methods, depending on the magnitude of the residual chlorine and the differentiation of chlorine fractions desired. Follow the directions for performing these determinations as described under "Residual Chlorine," above, p. 2415.

If desired, check the taste and odor quality of the chlorinated and dechlorinated samples by following the pertinent instructions given under "Taste and Odor," p. 2493, below. Dechlorinate with minimal amounts of  $\text{Na}_2\text{SO}_3$ .

**Field Determination.**—Follow the directions set forth in the preceding procedure with the following exceptions. Dose the first sample bottle with 1 drop standard chlorine solution, the second sample bottle with 2 drops, the third with 3 drops, and so on up the scale. Determine the residual chlorine by the orthotolidine-arsenite method.

Record the chlorine dosage, contact time, temperature, and the amount of free available, and/or combined, or total residual chlorine found in each bottle.

Chlorine demand, milligrams per liter

= milligrams per liter of chlorine added — milligrams per liter of residual chlorine.

### CHROMIUM <sup>2</sup>

Mercurous and mercuric ions yield a blue or violet-blue color with s-diphenylcarbazide but the reaction is not very sensitive at the specified acidity. A yellow color is produced both with Fe concentrations in excess of 1 mg. per liter, and with V. The V color fades rapidly to negligible proportions within 10 min., however.

Low chromate results may be obtained after storage in glass or polyethylene bottles. Therefore, promptness is desirable in undertaking the determinations of hexavalent and total Cr. Unscratched glassware cleaned with HCl or  $\text{HNO}_3$  should be reserved for this determination to guard against contamination from adsorbed Cr.

**Reagents.** Deionized Distilled Water or Redistilled Water.—These should be used for the preparation of all solutions and dilutions.

**Standard Chromium Solution.**—(a) Dissolve 0.1414 g.  $\text{K}_2\text{Cr}_2\text{O}_7$ , dried at  $110^\circ\text{C}$ ., in water and dilute to 1000 ml. (b) Dilute 20.00 ml. stock solution to 1000 ml. to form a standard solution containing 0.001 mg. hexavalent Cr per 1.00 ml. Prepare the standard solution daily.

**s-Diphenylcarbazide Reagent.**—(a) Dissolve 0.2 g. s-diphenylcarbazide (also called 1,5-diphenylcarbohydrazide) in 100 ml. 95% ethyl or isopropyl alcohol. (b) Cautiously mix 40 ml. concentrated  $\text{H}_2\text{SO}_4$  with 360 ml. water. (c) Combine solutions (a) and (b). The refrigerated solution is usable for a month, even though the color changes from colorless to tan.

**Sodium Sulfite Solution, 1.26 g. per 100 ml.**—Use 1 ml. to reduce 3.4 mg. hexavalent Cr to the trivalent state. Prepare daily.

**Sodium Azide Solution, 0.5 g. per 100 ml.**

**Sulfuric Acid, 1 + 1.**

## Potassium Permanganate, 0.1 N

**Procedure** Determination of Hexavalent Chromium—If necessary clarify the sample by centrifuging. Pipet a sample volume containing 0.0003 to 0.010 mg hexavalent Cr into a 50 ml Nessler tube or volumetric flask. Prepare a series of visual standards in the Cr range 0.00015 to 0.010 mg. Alternatively prepare the photometric calibration curve from Cr standards in the range 0.00025 to 0.020 mg for absorbance readings in a 5 cm cell and 0.010 to 0.100 mg for a 1 cm cell. Dilute the blank standards and sample to 50.0 ml, mix, add 2.5 ml *s*-diphenyl carbazide reagent and again mix thoroughly. Measure the absorbance at 540 mμ or make the visual comparison within 5 to 15 min of the reagent addition.

**Determination of Total Chromium**<sup>23</sup>—Pipet a sample volume containing 0.0003 to 0.010 mg Cr into a flask and add 5 ml 1 + 1 H<sub>2</sub>SO<sub>4</sub> and 1 ml Na<sub>2</sub>SO<sub>3</sub> solution. After 10 min standing insert 3 glass beads or Berl saddles, evaporate to fumes and fume for 15 min or until clear. Cool to room temperature and carefully dilute to 50 to 80 ml. Bring to a boil and add enough 0.1 N KMnO<sub>4</sub> drop by drop to insure a pink color throughout the 10 min boiling period. As the boiling continues add the Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> solution dropwise until the KMnO<sub>4</sub> color is discharged. Make the final Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> additions 2 min apart to avoid introducing an excessive amount of the reductant. Cool to room temperature and transfer the clear and colorless solution to a 50 ml Nessler tube or volumetric flask.

If necessary remove any suspended matter by filtration under suction through a sintered glass filter. Use a filter of coarse porosity for colorless solutions and of medium porosity when MnO<sub>2</sub> precipitate is present. Collect the filtrate in a 100 ml Nessler tube or volumetric flask to permit adequate washing of the filter.

Develop the color with *s*-diphenylcarbazide reagent, and complete the determination as described for hexavalent Cr. Prepare the photometric calibration curve by carrying a blank and Cr standards through the entire procedure.

Hexavalent or total Cr, milligrams per liter

$$= \frac{\text{milligrams of hexavalent or total Cr} \times 1000}{\text{milliliters of sample}}$$

COLOR<sup>24</sup>

The color method is based on the visual comparison of the water sample with a series of artificial standards. The method is applicable to most natural waters even though the shadings of some samples may vary somewhat from the standards. The standard unit is the color produced by 1 mg of platinum in association with 0.5 mg of cobalt in 1 liter of solution.

True color is due to dissolved organic material while apparent color results from the additional presence of suspended matter. For this reason the apparent color is higher than the true color.

No universally acceptable method for removing turbidity is available. Centrifuging should be tried first and in its failure to eliminate particles of small size filtration through paper or coagulation may be resorted to despite the known hazards of color removal. The method of turbidity removal should be identified in the report along with the color readings obtained. On account of these several considerations the results must be regarded as approximate. In spite of the dif-

<sup>23</sup> Lieber, M. J. *Am. Water Works Assn.* 48, 295, 1956.

facilities imposed by turbidity, the measurement of color is a useful procedure in the control of water treatment.

**Stock Color Solution.**—Dissolve 1.246 g.  $K_2PtCl_6$  and 1 g.  $CoCl_2 \cdot 6H_2O$  in distilled water containing 100 ml. concentrated HCl, and dilute to 1000 ml. with distilled water. This solution bears 0.500 g. Pt and 0.25 g. Co, and has a color value of 500 units, or 1.0 ml. = 0.5 unit. Platinum may be substituted for the  $K_2PtCl_6$  by dissolving 0.500 g. of the pure metal in aqua regia by means of heat. The  $HNO_3$  is removed by repeated evaporation to dryness on a water bath after adding excess concentrated HCl. The residue is then dissolved along with 1 g.  $CoCl_2 \cdot 6H_2O$  in the prescribed manner.

**Procedure.** Preparation of Permanent Color Standards in the Range of 5 to 70 Units.—Place 0.5, 1.0, 1.5, 2.0, 2.5, 3.0, 3.5, 4.0, 4.5, 5.0, 6.0, and 7.0 ml. stock color solution in 50-ml., tall-form Nessler tubes, and dilute to the mark with distilled water. Protect the standards from evaporation and contamination when not in use, and store away from strong light.

**Sample Evaluation.**—Fill the Nessler tube to the 50-ml. mark with the clear water sample, and compare the color with the standards by looking downward through the tubes against a pure white surface. If the color exceeds 70 units, dilute the sample with known proportions of distilled water until the color falls within the range of the standards. Record the color units within the ranges 1 to 50, 51 to 100, 101 to 250, and 251 to 500 to the nearest 1, 5, 10, and 20 units, respectively.

### SPECIFIC CONDUCTANCE<sup>2, 11, 24</sup>

**Standard Potassium Chloride Solution, 0.0100 N.**—Dissolve 0.7456 g. KCl, dried overnight at 110°C., in freshly boiled and cooled redistilled water, and dilute to 1000 ml. The specific conductance of this standard reference solution is 1411.8 micromhos per cm. at 25.0°C.

**Procedure.**—Select tubes of the proper dimensions to hold sufficient liquid for use with the available conductance cell. Place 4 tubes of standard 0.0100 N KCl and 2 tubes of each water sample in a water bath adjusted at 25°C. for 30 min. Rinse the conductance cell in 3 of the KCl tubes, and measure the resistance,  $R_1$ , of the solution in the fourth tube. Rinse the conductance cell very thoroughly with the water sample in the first tube, and record the reading,  $R_2$ , on the water in the second tube. Also observe to the nearest 0.1°C. the temperature of each standard and sample being measured.

$$\text{Specific conductance in micromhos per cm.} = \frac{1411.8 \times R_1}{R_2}$$

where  $R_1$  = resistance in ohms of the standard 0.0100 N KCl at 25.0°C., and  
 $R_2$  = resistance in ohms of the water sample at 25.0°C.

Routine resistance measurements can be made with sufficient precision and accuracy in the temperature range from 20° to 30°C. In such a case, the changing resistances,  $R_1$ , of the standard 0.0100 N KCl are measured throughout the operating temperature range used in the given laboratory. A graph is plotted of the resistance in ohms versus temperature in degrees C. This graph is then consulted for the resistance of the 0.0100 N KCl at the temperature at which the water sample,  $R_2$ , is measured, and substituted in  $R_1$  of the preceding equation.

<sup>24</sup> Wilcox, L. V., J. Am. Water Works Assn., 42, 775, 1950.

COPPER <sup>2+</sup>

The following interferences affect the cuprethol method 2 mg per liter chromate or dichromate 5 mg per liter chromic, 10 mg per liter Pb, or manganous or stannic, or uranyl, 20 mg per liter Al or Cd or CN, or Zn, or ferric, or mercuric or nitrite, or stannous 50 mg per liter ferrous 100 mg per liter sulfite, and 400 mg per liter Ca Mercurous Bi Co Ni and Ag must be absent

All glassware should be thoroughly cleaned by treatment with concentrated HCl to dissolve any adsorbed Cu

**Reagents** Deionized Distilled Water or Redistilled Water—These should be used for the preparation of all solutions and dilutions

**Standard Copper Solution**—Prepare the stock solution containing 0.100 mg Cu per 100 ml from the pure metal as described in (a) or from the salt as described in (b)

(a) Place 0.1000 g Cu foil in a beaker and dissolve in 3 ml concentrated HNO<sub>3</sub> and 3 ml water After dissolution add 1 ml concentrated H<sub>2</sub>SO<sub>4</sub> and expel the acids by heating Stop just short of complete dryness, take up the cooled residue in water and dilute to 1000 ml

(b) Dissolve 0.3930 g CuSO<sub>4</sub> · 5H<sub>2</sub>O in water and dilute to 1000 ml

(c) Dilute 50.00 ml stock solution (a) or (b) to 1000 ml to form a standard solution containing 0.005 mg Cu per 100 ml Prepare daily

**Cuprethol Reagent**—(a) Dissolve 4 g diethanolamine in 200 ml methyl alcohol Refrigerate and prepare monthly (b) Dissolve 3.0 ml CS<sub>2</sub> in 200 ml methyl alcohol Refrigerate and prepare monthly (c) Mix equal volumes of solution (a) and (b) to form the cuprethol reagent Stopper tightly to maintain stability for a week Discard the reagent that causes a turbidity on addition to a clear Cu solution

**Sodium Pyrophosphate Decahydrate Solution**, 30 g per liter

**Sodium Acetate Solution**—Dissolve 400 g NaC<sub>2</sub>H<sub>3</sub>O<sub>2</sub> · 3H<sub>2</sub>O in 600 ml water by heating

**Methyl Alcohol.**

**Isoamyl Alcohol**

**Ethyl Alcohol.**

**Hydrochloric Acid, 1 + 1.**

**Procedure**—Pipet 2 portions of the sample, containing less than 0.05 mg Cu into beakers, and dilute to 100 ml if necessary When the sample contains color or turbidity use the second portion as a sample blank to which all reagents are added except cuprethol Substitute 2 ml methyl alcohol for the cuprethol in this situation

Prepare a blank and a series of Cu standards in 100 ml volume with the following quantities of standard solution (c) 0, 0.50, 1.00, 2.00, 3.00, 4.00, 6.00, 8.00, and 10.0 ml Treat the blank and standards exactly as the sample throughout the procedure Mixing after each addition, introduce 0.5 ml 1 + 1 HCl (omit the HCl if used previously for sample preservation), 2 ml Na<sub>4</sub>P<sub>2</sub>O<sub>7</sub> solution, and enough NaC<sub>2</sub>H<sub>3</sub>O<sub>2</sub> solution (frequently 10 ml suffices) to adjust the pH range to 5 to 6 After 5 min add 1 ml cuprethol reagent (c) Within 10 to 30 min read the absorbance at 435 mμ in a 5 cm cell, or visually match the colors in Nessler tubes Set the photometric null of each sample with the special sample blank

**Extraction Finish.**—For visual determinations on turbid samples, add 5 ml. isoamyl alcohol, and extract the developed color by inverting the Nessler tube for 3 min. Compare the colors in the organic layers of the sample and the standards. If necessary, break up any emulsion by gently stirring a few drops ethyl alcohol into the organic layer with a glass rod.

**Simplified Field Determination.**—When interfering ions are absent, the ferrous and ferric concentrations do not exceed 0.6 mg. per liter and 0.3 mg. per liter, respectively, and the pH range falls between 1.5 and 9, add 1 ml. cuprethol reagent (c) to 100 ml. sample, mix, and compare immediately against simultaneously prepared standards.

$$\text{Cu, milligrams per liter} = \frac{\text{milligrams of Cu} \times 1000}{\text{milliliters of sample}}$$

### CYANIDE<sup>2, 26</sup>

Although distillation fails to control all interference, the benefits in many situations are such that omission should never be considered unless the CN results are shown to be identical, both with and without distillation. Most complex cyanides are converted to simple CN by distillation, conversion to simple CN being hastened in the presence of  $\text{HgCl}_2$  and  $\text{MgCl}_2$ . Analytical precision is questionable unless all cyanides are, or have been, converted to simple CN. Complexed cyanides vary in analytical response from those, like Zn and Cd, that approach the behavior of simple CN, to relatively stable complexes such as Co, certain cuprous and cupric complexes, and possibly others that are not likely to yield quantitative results with current methods. Results are affected by time and conditions existing during complex formation because a stable complex may require appreciable time to form. For this reason, 2 reflux-distillation periods are recommended to classify the type of CN in the original sample. If no detectable CN is recovered during the second hour of reflux-distillation, the sample contains simple CN or easily hydrolyzed complexed cyanides. Analytical recovery is likely to be good. If a measurable quantity of CN appears during the second hour of reflux-distillation, relatively stable complexed cyanides are present and analytical recovery is likely to be low.

The following interferences should be removed before distillation is undertaken. Sulfide should be completely precipitated by treating the alkaline sample at pH 11.0 with small amounts of  $\text{PbCO}_3$ , filtering, and washing the precipitate. Oxidants should be reduced with  $\text{Na}_2\text{SO}_3$  (12.6 g. per liter) until a negative test is obtained with starch-iodide paper. Samples containing fatty acids should be acidified to pH 6 to 7 with acetic acid, and then quickly extracted with isooctane, hexane, or  $\text{CHCl}_3$  (listed in the order of preference) with a solvent volume equal to one-fifth of the sample volume.

Thiocyanate is a major interference in the direct colorimetric determination. Cyanate, glycine, urea, and other compounds that can hydrolyze to form CN during the analysis are lesser interferences. Color- and turbidity-forming agents also interfere in the colorimetric method. Since the colorimetric procedure is affected by the sample's buffering capacity, distillation offers a simple means of coping with this important variable and such interferences as thiocyanate, cyanate, glycine, urea, and turbidity.

Samples that cannot be analyzed promptly should be treated with NaOH to

<sup>26</sup> Ludzack, F. J., *et al.*, Anal. Chem., 26, 1784, 1954.

raise the pH to 11.0 or higher refrigerated, and the determination begun as soon as possible

**Reagents for Distillation** Mercuric Chloride Solution, 8 g per 200 ml

Magnesium Chloride Hexahydrate Solution, 51 g per 100 ml

Sulfuric Acid Concentrated

Sodium Hydroxide, 1 N

**Reagents for Titrimetric Method** Standard Silver Nitrate Titrant, 0.0192 N—Dissolve 3.261 g  $\text{AgNO}_3$  and dilute to 1000 ml with distilled water. Standardize as described in Chloride above p. 2414 against standard NaCl solution and  $\text{K}_2\text{CrO}_4$  indicator. The equivalence of 0.0192 N  $\text{AgNO}_3$  is 100 mg CN per 100 ml.

*p*-Dimethylaminobenzalrhodamine Indicator, 0.02 g + 100 ml acetone

Sodium Hydroxide, 1 N

**Reagents for Colorimetric Method** Standard Cyanide Solution—(a) Dissolve 2.51 g KCN in distilled water and dilute to 1000 ml. Standardize weekly by diluting 10.00 ml stock KCN solution to 250 ml with distilled water, adjusting the pH to 11.0 or above with 1 N NaOH, adding 0.5 ml *p*-dimethylaminobenzalrhodamine indicator and titrating with standard 0.0192 N  $\text{AgNO}_3$  to the first change in color from canary yellow to a salmon tint. Determine the titration blank required for the same volumes of 1 N NaOH and distilled water. Calculate the CN content of the stock solution by the following equation:

$$\text{CN, milligrams per liter} = \frac{(A - B) \times 1000}{\text{milliliters of KCN taken}}$$

where  $A$  = milliliters of titration for KCN aliquot

$B$  = milliliters of titration for blank

(b) Dilute 10.00 ml stock solution with distilled water to 1000 ml for an intermediate dilution. (c) Then dilute 10.00 ml intermediate dilution to 100 ml to form a standard solution containing 0.001 mg CN per 100 ml. Prepare the intermediate and standard solutions daily.

**Mixed Pyridine Pyrazolone Reagent**—(a) Add 1.5 g 1-phenyl-3-methyl-5-pyrazolone in 250 ml hot distilled water. Stir as the solution cools to room temperature.

(b) Dissolve 0.025 g bis-pyrazolone [3,3-dimethyl-1,1-diphenyl-4,4-bis-2-pyrazolene-5,5-dione] in 25 ml pyridine by stirring for several minutes. Prepare daily. (c) Mix 125 ml solution (a) with all of solution (b). Prepare daily.

**Chloramine T Solution**—One g + 100 ml distilled water. Prepare daily. Reject any dry reagent that fails to dissolve promptly upon mixing in the designated volume of water.

**Disodium Hydrogen Phosphate Solution**—Five g  $\text{Na}_2\text{HPO}_4$  + 100 ml distilled water.

*n*-Butyl Alcohol

Acetic Acid, 1 + 4

Sodium Hydroxide, 6 N

**Procedure** Distillation<sup>27</sup>—Assemble the distillation apparatus as shown in Fig. 48.5. Pour 50 ml 1 N NaOH into the gas washer of 100 to 250 ml liquid capacity and if necessary, dilute with distilled water to cover the spiral *D*. Connect the entire train including a trap *E* to a water aspirator, *F*, and adjust the suction to

<sup>27</sup> Serfass, E. J., *et al.*, *Plating* 39, 267, 1952.

maintain an air-flow rate through the unit just below the point of bubble coalescence in the spiral, *D*. Approximately 1 bubble per second is satisfactory. In the case of a potable water meeting USPHS drinking water standards for CN, take a sample volume of 500 ml. and add to the 1-liter boiling flask, *B*. Use a smaller aliquot diluted to 250 ml. if the sample contains more than 10 mg. per liter of CN. Through the air-inlet tube, *A*, add 20 ml.  $\text{HgCl}_2$  solution and 10 ml.  $\text{MgCl}_2$  solution. Wash the tube with distilled water, and allow the air flow to

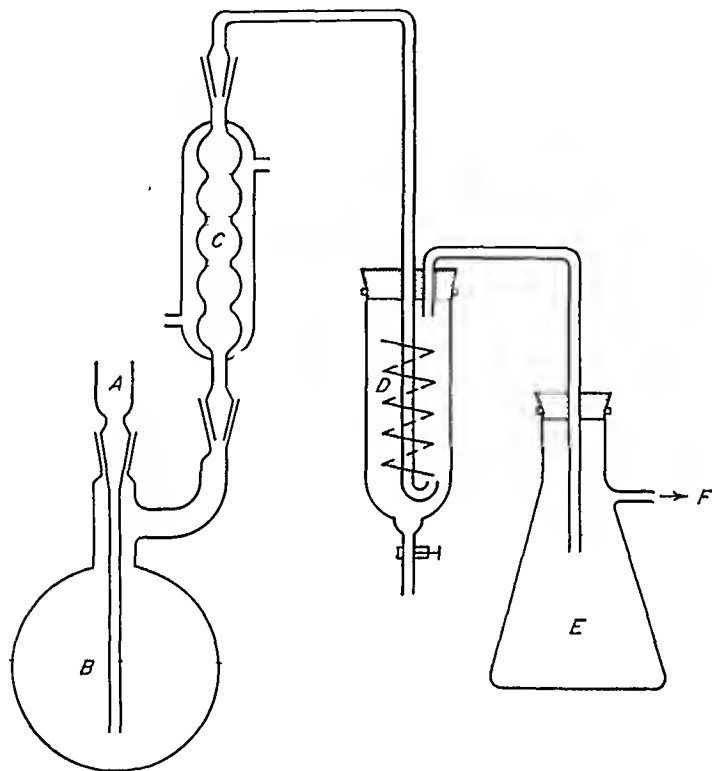


FIG. 48-5. Cyanide Distillation Apparatus.

mix the flask contents for 3 min. Slowly and carefully introduce 5 ml. concentrated  $\text{H}_2\text{SO}_4$  into the distilling flask. Again wash the air-inlet tube with distilled water. Heat the flask at a rate that will not cause expansion of trapped air, thereby producing an unusual rise of liquid into the air-inlet tube. Then adjust the heating to secure a good reflux rate without forming a condensation line above one-quarter of the condenser, *C*. If the initial heating rate is excessive, and the liquid backs up into the air-inlet tube, stop the heating and cool the flask momentarily. After refluxing and distilling for 1 hr., turn off the heat, but maintain the air flow for an additional 15 min. Open the pinch clamp and drain the gas washer contents into a 250-ml. volumetric flask, and dilute to the mark by washing the scrubber. Refill the gas washer with another charge of 50 ml. 1 *N*  $\text{NaOH}$ . Repeat the reflux-distillation on the same sample for an additional 1-hr. period. Determine the CN concentration of both distillates first by the titrimetric

method to ascertain the order of magnitude, and then colorimetrically, when the CN concentration is low

**Titrimetric Method**<sup>28</sup>—Select a distillate or sample volume that will require less than 10 ml titrant. When the CN content falls below 50 mg per liter, transfer 200 ml distillate or sample to a flask or white porcelain casserole. If necessary, add 1 N NaOH to the sample until the pH exceeds 11. Introduce 0.5 ml *p*-dimethylaminobenzalrhodanine indicator, and titrate with standard 0.0192 N AgNO<sub>3</sub> until the initial canary yellow changes to a salmon hue. If the titration interval exceeds 3 to 5 min, replenish the indicator in order to replace the amount decomposing in the high pH medium. Determine the titration blank required for the same volumes of 1 N NaOH, indicator, and distilled water

$$\text{CN, milligrams per liter} = \frac{(A - B) \times 1000}{\text{milliliters of sample}} \times \frac{C}{D}$$

where *A* = milliliters of titration for distillate or sample,

*B* = milliliters of titration for blank

The ratio *C/D* applies only when a sample is distilled, the volume is then made up to *C* and an aliquot, *D*, is taken from it for titration

**Colorimetric Method**<sup>29</sup>—Select a distillate aliquot or sample volume containing 0.0002 to 0.001 mg CN. In the case of a potable water, free of interference and meeting USPHS drinking water standards for CN, measure a sample volume of 15.0 ml into a 25 by 20 cm test tube. Prepare a blank and a series of CN standards (0.0002, 0.0004, 0.0006, 0.0008, and 0.0010 mg) in test tubes of the same size. Treat the blank and standards exactly as the sample throughout the procedure. Neutralize the sample or distillate, blank, and standards with 1 + 4 acetic acid or 6 N NaOH to pH 6 to 7. Add 0.2 ml chloramine T solution, cap with a clean rubber stopper, and mix by inverting several times. After 2 min, add 5.0 ml mixed pyridine-pyrazolone reagent (c), stopper, and mix by inversion. Dilute to 25.0 ml with distilled water and mix again. Following 20 min of color development, read the absorbance at 620 mμ in a 1 cm cell.

Increase the sensitivity of the determination, and overcome turbidity interference by extracting the color as follows: after 20 min of color development, add 1 ml Na<sub>2</sub>HPO<sub>4</sub> and 10 ml of carefully measured *n*-butyl alcohol, stopper the tube and mix by inversion, add more Na<sub>2</sub>HPO<sub>4</sub> solution if the emulsion fails to break within 1 to 3 min, and mix again, measure the absorbance of the alcohol layer at 630 mμ, vary the sample and butyl alcohol volumes to increase the sensitivity still more.

$$\text{CN, milligrams per liter} = \frac{A \times 1000}{\text{milliliters of sample}} \times \frac{B}{C}$$

where *A* = milligrams of CN found photometrically. The ratio *B/C* applies when a sample is distilled, the volume then made up to *B*, and an aliquot, *C*, is taken from it for color development.

<sup>28</sup> Ryan, J. A., and Culshaw, G. W. *Analyst*, **69**, 370, 1944.

<sup>29</sup> Epstein, J. *J. Anal. Chem.*, **19**, 272, 1947.



FLUORIDE <sup>2</sup>

Because the colorimetric methods for F are susceptible to color, turbidity, and chemical interference, distillation of unfamiliar waters is advisable for a reliable determination. The distillation should be arrested before the temperature exceeds 180°C., otherwise serious SO<sub>4</sub> carry-over will result.

Two methods of color development and measurement are described. The visual method entails a 1-hr. color development period, whereas the color produced in the second method can be measured photometrically without any delay. Temperature and the measurement of the reagents play critical roles in the color development by both the visual and photometric methods. The blank, F standards, and sample, therefore, should be adjusted to the same temperature before the reagents are introduced with volumetric pipets. Residual chlorine interferes severely in both the visual and photometric methods, and must be eliminated with NaAsO<sub>2</sub> or Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>. The addition of Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> should be kept below 100 mg. per liter, in order to prevent the formation of an interfering colloid or precipitate. The visual zirconium-alizarin method is affected by the following interferences in the indicated concentrations: 400 mg. per liter alkalinity as CaCO<sub>3</sub>, 0.25 mg. per liter trivalent Al, 2000 mg. per liter Cl, 2 mg. per liter ferric ion, 1.0 mg. per liter (NaPO<sub>3</sub>)<sub>6</sub>, 5 mg. per liter PO<sub>4</sub>, and 300 mg. per liter SO<sub>4</sub>. The photometric method is affected by the following interferences in the specified amounts: 5000 mg. per liter alkalinity as CaCO<sub>3</sub>, 0.1 mg. per liter trivalent Al, 10 mg. per liter ferric ion, 7000 mg. per liter Cl, 1.0 mg. per liter (NaPO<sub>3</sub>)<sub>6</sub>, 16 mg. per liter PO<sub>4</sub>, and 200 mg. per liter SO<sub>4</sub>. In both methods the first 3 substances listed depress the true F reading by 0.10 mg. per liter, while the remaining 4 substances increase the F by 0.10 mg. per liter, when the F is determined at the 1.0 mg. per liter level.

**Reagents.** **Standard Fluoride Solution.**—(a) Dissolve 0.2210 g. NaF, dried at 105°C., in distilled water, and dilute to 1000 ml. (b) Dilute 100.0 ml. stock solution to 1000 ml. with distilled water, to give a standard solution containing 0.010 mg. F per 1.00 ml.

**Sodium Arsenite Solution,** 5.0 g. NaAsO<sub>2</sub> per liter.

**Sulfuric Acid,** Concentrated.

**Silver Sulfate.**

**Reagents for Visual Method.** **Mixed Zirconium-Alizarin Reagent.**—(a) Add 101 ml. concentrated HCl to 300 ml. distilled water. Carefully add 33.3 ml. concentrated H<sub>2</sub>SO<sub>4</sub> to 400 ml. distilled water. Mix the 2 solutions after both have cooled. (b) Dissolve 0.30 g. ZrOCl<sub>2</sub>·8H<sub>2</sub>O in 50 ml. distilled water. Dissolve 0.07 g. sodium alizarin monosulfonate (also called Alizarin Red S) in 50 ml. distilled water, and slowly stir into the zirconium solution. After the mixed solution clears, add solution (a), and dilute to 1000 ml. with distilled water. Mix thoroughly and use after the reagent color changes from red to yellow within an hour. Store away from direct sunlight.

**Reagents for Photometric Method.** **Mixed Reagent for Photometric Determination.**—(a) Dissolve 0.958 g. 4,5-dihydroxy-3-(*p*-sulfophenylazo)-2,7-naphthalenedisulfonic acid trisodium salt in distilled water and dilute to 500 ml. (b) Dissolve 0.133 g. ZrOCl<sub>2</sub>·8H<sub>2</sub>O in 25 ml. distilled water, add 350 ml. concentrated HCl, and dilute to 500 ml. with distilled water. (c) Prepare the mixed reagent from equal volumes of solutions (a) and (b). (d) Prepare the photometric reference solution by mixing 10 ml. solution (a), 103 ml. distilled water, and 7 ml. concentrated HCl.

**Procedure** Disillation<sup>30</sup>—Use the borosilicate glass distillation apparatus illustrated in Fig 48 6 however, replace the 24/40 glass stopper on the distilling flask with a rubber stopper holding a thermometer that reads in the 180°C range, and is immersed in the acid solution at all times Measure 400 ml distilled water into

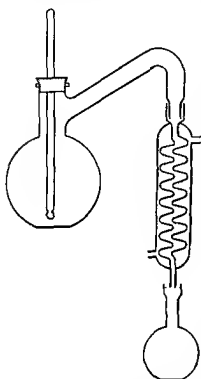


FIG 48 6 Distillation Apparatus for Fluoride Phenol Selenium Ammonia and Albuminoid Nitrogen Determinations (The Illustrated Thermometer in the Flask is Required Only in the Fluoride Determination The Rubber Stopper Containing the Thermometer Can be Replaced with a Glass Stopper for the Other Distillations)

the 1 liter distilling flask, together with 25 to 35 glass beads Carefully introduce with mixing 200 ml concentrated  $H_2SO_4$  and make certain that the water and acid are homogeneously dispersed Insert into the flask the rubber stopper with the thermometer, and distill until the temperature of the flask contents reaches 179°C but guard against a penetration beyond 180°C Reject the distillate

After the flask contents cool to 120°C or lower add 300 ml sample to the distilling flask, and mix the acid and sample completely with a stirring rod Precipitate interfering amounts of chloride in the sample by adding solid  $Ag_2SO_4$  at the rate of 5 mg  $Ag_2SO_4$  per mg Cl Resume distillation until the temperature of the flask contents again reaches 179°C but does not exceed 180°C Collect and save the distillate

Use the  $H_2SO_4$  solution in the flask repeatedly until interferences appear in the distillate Check periodically for this possibility by distilling known F solutions After the distillation of high F samples flush the entire apparatus by distilling 300 ml distilled water before undertaking a sample of low F content

**Visual Color Matching Method**<sup>31, 32</sup>—Select a distillate aliquot or a volume of clear sample containing 0 010 to 0 140 mg F Reduce any residual chlorine in the sample by adding 1 drop (0 05 ml) or more  $NaAsO_2$  solution If necessary, dilute with distilled water to the mark of a 100 ml Nessler tube In 100 ml Nessler tubes prepare a series of F standards in the 0 000 to 0 140 mg range so that the sample falls within 0 005 mg of the F standard immediately above and the F standard

immediately below Bring the standards and the clear sample to room temperature and maintain a constant temperature ( $\pm 2^\circ C$ ) throughout the color development period With a volumetric pipet add 5 ml mixed zirconium alizarin reagent (b) mix well, and match the sample with the standards after 1 hour

**Photometric Method**<sup>33</sup>—Select a distillate aliquot or a volume of clear sample containing 0 005 to 0 070 mg F Reduce any residual chlorine in the sample by adding 1 drop (0 05 ml) or more  $NaAsO_2$  solution If necessary, dilute with dis

<sup>30</sup> Bellack, E, J Am Water Works Assn, 50, 530 1958

<sup>31</sup> Sanchis J M, Ind Eng Chem, Anal Ed, 6, 134, 1934

<sup>32</sup> Scott R D J Am Water Works Assn 33, 2018, 1911

<sup>33</sup> Bellack F and Schouboe P J Anal Chem, 30, 2032, 1958

tilled water to 50.0 ml. Prepare a blank and a series of F standards (0.010, 0.030, 0.050, 0.060, and 0.070 mg.) in 50.0-ml. volume with distilled water. Treat the blank and standards exactly as the sample throughout the procedure. Bring the blank, standards, and sample to the same temperature. With a volumetric pipet add 10 ml. mixed reagent for photometric determination (c), mix well, and read the absorbance at 570  $m\mu$  in a 1- or 2-cm. cell against the photometric reference solution (d).

$$F, \text{ milligrams per liter} = \frac{A \times 1000}{\text{milliliters of sample}} \times \frac{B}{C}$$

where  $A$  = milligrams of F found visually or photometrically. The ratio  $B/C$  applies only when a sample is distilled, the volume then made up to  $B$ , and an aliquot,  $C$ , taken from it for color development.

### GREASE AND OILY MATTER

No standard method for oil and grease is described here because of the impossibility of specifying a solvent that is capable of extracting all important oils, greases, and waxes.

### HARDNESS <sup>2,11</sup>

Calculation of the hardness from the individual gravimetric determinations remains the generally accepted method. The concentration of each hardness-producing cation is converted to the equivalent  $\text{CaCO}_3$  concentration, and the resulting  $\text{CaCO}_3$  concentrations are then totaled. The following factors must be multiplied by the determined concentration (milligrams per liter) of the indicated cation to obtain the  $\text{CaCO}_3$  equivalent in milligrams per liter: Ca, 2.497; Mg, 4.116; Sr, 1.142; Fe, 1.792; Al, 3.710; Zn, 1.531; Mn, 1.822. The report should show which cations were involved in the computation of the total hardness. The total hardness may represent the  $\text{CaCO}_3$  equivalent of only Ca and Mg, or all or some of the cations cited above.

### COMPLEXOMETRIC METHOD <sup>13, 14, 15, 34, 35</sup>

When a 25-ml. sample is diluted to 50 ml. with distilled water, the following individual interferences in the specified concentrations can be tolerated in the presence of one of the 3 common inhibitors. In the presence of 0.25 g. NaCN the maximum tolerable concentrations are more than 30 mg. per liter for Cu or Fe, more than 20 mg. per liter for Co or Ni, and 20 mg. per liter for Al, while manganous ion titrates like hardness. In the presence of 1 ml.  $\text{Na}_2\text{S}$  solution, the maximum tolerable concentrations are 200 mg. per liter for Zn, 20 mg. per liter for Al or Cd or Cu or Pb, 10 mg. per liter for polyphosphate, 5 mg. per liter for Fe, 1 mg. per liter for manganous ion, and 0.3 mg. per liter for Co or Ni. In the presence of 1 ml.  $\text{NH}_2\text{OH}\cdot\text{HCl}$  solution the maximum tolerable concentrations are 20 mg. per liter for Al or Fe, 1 mg. per liter for manganous ion, 0.3 mg. per liter for Cu, while Co and Ni must be absent. Barium and Sr titrate as hardness in the presence of all 3 inhibitors.

Cadmium, Pb, and Zn titrate like hardness in the presence of NaCN or  $\text{NH}_2\text{OH}\cdot\text{HCl}$ . The higher oxidation states of Mn can be reduced to the manga-

<sup>34</sup> Betz, J. D., and Noll, C. A., J. Am. Water Works Assn., 42, 49, 1950.

<sup>35</sup> Diehl, H., Goetz, C. A., and Hach, G. C., J. Am. Water Works Assn., 42, 40, 1950.

nous form by  $\text{NH}_2\text{OH}\cdot\text{HCl}$  reagent Manganous interference can then be eliminated by the addition of 1 or 2 small crystals of  $\text{K}_4\text{Fe}(\text{CN})_6$  before the titration is undertaken

All the prepared solutions are subject to deterioration, and should be kept tightly stoppered. A poor or off color end point suggests the need of an appropriate inhibitor or the replacement of an old batch of indicator. The titration should be performed at room temperature to avoid the slow reaction occurring at cold temperatures and decomposition of the indicator in hot water. Moreover, the titration should be completed within 5 min. to prevent  $\text{CaCO}_3$  precipitation at a pH of 10.0 to 10.1. Sample volumes of 100 to 1000 ml can be taken when the hardness falls below 100 mg per liter  $\text{CaCO}_3$ , in which case the reagent volumes can be proportionately increased above those cited in the procedure. Samples of known excessive hardness can be determined by adding 90% or more of the EDTA titrant before the pH is adjusted to 10.0 to 10.1 with the buffer.

**Reagents** Standard EDTA Titrant, 0.01 M (0.02 N).—Dissolve 3.72 g disodium ethylenediaminetetraacetate dihydrate (EDTA), and dilute to 1000 ml with distilled water. Standardize against standard Ca solution under exactly the same conditions (similar volumes of buffer, final solution, and indicator quantity) as for the titration of water samples. Pipet a volume of standard Ca solution that approximates either the average or median (whichever is applicable) hardness usually prevailing in the water samples determined in the particular laboratory. The equivalence of 0.01 M (0.02 N) EDTA titrant is 1.00 mg  $\text{CaCO}_3$  per 1.00 ml.

**Standard Calcium Solution**—Suspend 1.000 g  $\text{CaCO}_3$ , dried at  $105^\circ\text{C}$  overnight or longer, in 200 ml distilled water contained in a 1 liter, borosilicate-glass, volumetric flask. Through a funnel, carefully add small amounts of 1 + 1 HCl until all the  $\text{CaCO}_3$  dissolves. Guard against the loss of  $\text{CaCO}_3$  because of vigorous and uncontrolled effervescence. After the  $\text{CaCO}_3$  has dissolved, boil off the  $\text{CO}_2$  for a few minutes, cool and neutralize the solution to methyl red indicator with 3 N  $\text{NH}_4\text{OH}$ . Dilute to the mark with distilled water. The equivalence of this solution is 1.000 mg  $\text{CaCO}_3$  per 1.00 ml.

**Buffer Solution**—Dissolve 67.5 g  $\text{NH}_4\text{Cl}$  in 570 ml concentrated  $\text{NH}_4\text{OH}$  and dilute to 950 ml with distilled water. Dissolve 3.120 g  $\text{MgSO}_4\cdot 7\text{H}_2\text{O}$  and 4.716 g disodium ethylenediaminetetraacetate dihydrate in 50 ml distilled water and add to the  $\text{NH}_4\text{OH}/\text{NH}_4\text{Cl}$  solution. Keep this solution tightly stoppered to prevent loss of  $\text{NH}_3$  or absorption of atmospheric  $\text{CO}_2$  and acid fumes.

**Sodium Sulfide Inhibitor Solution**.—This contains 5.0 g.  $\text{Na}_2\text{S}\cdot 9\text{H}_2\text{O}$  or 3.7 g  $\text{Na}_2\text{S}\cdot 5\text{H}_2\text{O}$  per 100 ml.

**Hydroxylamine Hydrochloride Solution**—Dissolve 4.5 g  $\text{NH}_2\text{OH}\cdot\text{HCl}$  in 100 ml 95% ethyl or isopropyl alcohol. (If desired, add 0.5 g Chrome Black T to this solution to make a combined inhibitor indicator solution.)

**Indicator**—Either a solid (a) or a liquid (b) formulation is satisfactory. (a) Grind together in a mortar 0.5 g Eriochrome Black T and 100 g NaCl to a 40 to 50 mesh. (b) Dissolve 0.5 to 1.0 g Eriochrome Black T in 100 g triethanolamine or ethylene glycol monomethyl ether.

**Phenolphthalein Indicator.**

Hydrochloric Acid, 1 N.

Sodium Hydroxide, 1 N.

Sodium Cyanide.

**Procedure**—Select a sample volume (preferably 25 or 50 ml) that will require less than 15 ml of titrant. Pipet the sample into a white porcelain casserole or

flask, and dilute to 50 ml. with distilled water. (If the sample contains an interfering amount of suspended or colloidal organic matter, place the aliquot in a platinum dish, evaporate to dryness on a steam bath, ignite the residue at 600°C. until the organic material is destroyed. Take up the residue in 20 ml. 1 *N* HCl, neutralize to phenolphthalein indicator with 1 *N* NaOH, and dilute to 50 ml. with distilled water.) Add whatever inhibitor may be necessary (0.25 g. NaCN, or 1 ml. Na<sub>2</sub>S solution, or 1 ml. NH<sub>2</sub>OH·HCl solution) to overcome any known interference, and mix. Add 1 to 2 ml. buffer solution, or a volume sufficient to produce a pH of 10.0 to 10.1, and mix. Add 1 to 2 drops indicator solution, or 0.2 g. powdered indicator mixture. Stirring constantly, titrate with standard 0.01 *M* EDTA until the last trace of purple disappears and the color turns a bright blue. Prepare a color comparison blank with distilled water by adding the quantities of inhibitor, buffer, and indicator used in the sample titration.

$$\text{CaCO}_3, \text{ hardness as milligrams per liter} = \frac{A \times B \times 1000}{\text{milliliters of sample}}$$

where *A* = milliliters of titration for sample,

*B* = milligrams of CaCO<sub>3</sub> equivalent to 1.00 ml. of EDTA titrant.

### IRON <sup>2, 11</sup>

The following ions interfere in the phenanthroline method: Cr; more than 2 mg. per liter Ni; Cu or Co in excess of 5 mg. per liter; Zn concentrations 10 times greater than Fe; and large amounts of such anions as PO<sub>4</sub>, F, citrate, tartrate, and oxalate, which may retard or impair color development by complexing Fe. Molybdate, Ag, Bi, Cd, and Hg are precipitated by 1,10-phenanthroline. The initial boiling with HCl converts polyphosphates to PO<sub>4</sub>, and eliminates potential interference from polyphosphates, cyanide, and nitrite. Interference due to small mercuric and Cd concentrations can be minimized through the addition of excess phenanthroline. The milky condition produced by Mo can be rectified by raising the pH above 5.5. Augmenting the quantity of NH<sub>2</sub>OH·HCl may correct the deleterious effect of strong oxidants.

The Fe range of the method may be extended by increasing the volume of phenanthroline reagent applied. Thus, 10 ml. phenanthroline reagent will enable Fe determinations up to 0.5 mg. in 100 ml. of final solution. Stopped color standards prepared for visual comparison in Nessler tubes are stable up to 3 months when protected from strong light. All glassware should be thoroughly cleaned by treatment with concentrated HCl to dissolve any adsorbed Fe.

**Reagents.** **Standard Iron Solution.**—Prepare the stock solution containing 0.200 mg. Fe per 1.00 ml. from the pure metal as described in (a) or from Mohr's salt as described in (b). (a) Dissolve 0.2000 g. clean Fe wire in 20 ml. 6 *N* H<sub>2</sub>SO<sub>4</sub>, and dilute to 1000 ml. with distilled water. (b) Dissolve 1.404 g. Fe(NH<sub>4</sub>)<sub>2</sub>(SO<sub>4</sub>)<sub>2</sub>·6H<sub>2</sub>O in 50 ml. distilled water and 20 ml. concentrated H<sub>2</sub>SO<sub>4</sub>, add 0.1 *N* KMnO<sub>4</sub> dropwise to impart a faint but persistent pink color, and dilute to 1000 ml. with distilled water. (c) Dilute 50.00 ml. stock solution to 1000 ml. with distilled water to form a standard solution containing 0.010 mg. Fe per 1.00 ml. Prepare daily. (d) Dilute 5.00 ml. stock solution to 1000 ml. with distilled water to form a standard solution containing 0.001 mg. Fe per 1.00 ml. Prepare daily.

**1,10-Phenanthroline Monohydrate Reagent.**—Dissolve 0.1 g. in 100 ml. distilled water containing 2 drops concentrated HCl. Not more than 0.1 mg. Fe can be determined satisfactorily with 1 ml. of this reagent.

**Ammonium Acetate Buffer Solution**—Dissolve 200 g  $\text{NH}_4\text{C}_2\text{H}_3\text{O}_2$  in 150 ml distilled water add 700 ml glacial acetic acid and dilute to 1 liter

**Hydroxylamine Hydrochloride Solution** 10 g per 100 ml

**Hydrochloric Acid Concentrated**

**Procedure Preliminary Sample Treatment Total Iron**—Measure 2 portions well mixed sample containing 0.005 to 0.1 mg Fe into 125 ml flasks or beakers. When the sample contains color or turbidity use the second portion as a sample blank to which all reagents are added except the phenanthroline. Substitute distilled water for the phenanthroline in this situation

If necessary remove interfering amounts of color or organic matter by wet ashing as described under Cadmium p 2408 above or dry ashing at temperatures not exceeding 700°C Carry a reagent blank through the same procedural steps

**Dissolved Iron**—Decant the supernatant from a settled sample and pass through a cellulose acetate membrane filter or an ashless fine textured retentive filter paper Reject the initial 25 ml filtrate Pipet a volume of the filtrate containing 0.005 to 0.1 mg Fe into a 125 ml flask or beaker

**Color Development**—Prepare a series of visual standards by measuring the following amounts of standard Fe solutions (d) and (c) into 125 ml flasks or beakers 0.005 0.010 0.020 0.030 0.040 0.050 0.060 0.070 0.080 and 0.100 mg Alternatively prepare the photometric calibration curve from the following Fe standards 0.010 0.020 0.030 0.040 and 0.050 mg for absorbance readings in a 5 cm cell and a final solution volume of 50 ml and 0.0050 0.100 0.150 0.200 and 0.250 mg for a 1 cm cell Dilute the blank and standards in 125 ml flasks or beakers to 50 ml with distilled water

To the total Fe or dissolved Fe sample blank and Fe standards add 2 ml concentrated HCl 1 ml  $\text{NH}_2\text{OH}$  HCl solution several beads and boil until the volume is reduced to 15 to 20 ml Transfer the cooled solution to a 50 or 100 ml volumetric flask or Nessler tube add 10 ml  $\text{NH}_4\text{C}_2\text{H}_3\text{O}_2$  buffer and 5 ml 1% phenanthroline reagent dilute to the mark with distilled water and mix well After 10 to 15 min read the absorbance at 510 m $\mu$  or visually match the colors in 100 ml tall form Nessler tubes Set the photometric null of each sample with the special sample blank

**Ferrous Ion**—Develop the color at the time of sample collection as described in Collection of Samples p 2393 above Read the absorbance at 510 m $\mu$  or visually match the colors in 100 ml Nessler tubes Calculate the sample volume as follows

Ferrous sample volume = total volume of bottled sample including reagents - 15 ml added reagents

$$\text{Fe milligrams per liter} = \frac{\text{milligrams of Fe} \times 1000}{\text{milliliters of sample}}$$

## LEAD<sup>2</sup>

Stannous Bi and Tl ions are the principal interferences in the dithizone extraction of Pb in a cyanide medium at pH 8 to 9 although these interferences seldom occur in potable waters The following dithizone modification is designed to overcome interference from nominal amounts of Cu Fe and Zn and is suitable for the photometric or visual determination of Pb in potable waters free from appreciable organic matter The sensitivity of the method requires the thorough cleansing of all glassware with dilute  $\text{HNO}_3$  followed by rinses with Pb free water

and dithizone solution. A wise precaution against contamination is the segregation of the glassware used for the Pb determination. As in the case of all dithizone methods, the photosensitivity of dithizone and dithizonates imposes the necessity for promptly performing the extractions out of the range of strong light. Carbon tetrachloride can be substituted for  $\text{CHCl}_3$  as the organic solvent for the preparation of dithizone solutions and extractions. Chloroform,  $\text{CCl}_4$ , and reagents of a grade satisfactory for dithizone work should be used exclusively.

A procedure for eliminating interfering amounts of organic matter is described in "General Procedure for Removal of Organic Matter Interference," p. 2408, above, under "Cadmium."

Samples destined for extended transport to the laboratory should be preserved with concentrated HCl at the rate of 5 ml. per liter of sample, to prevent serious adsorption losses.

**Reagents. Deionized Distilled Water or Redistilled Water.**—These should be used for the preparation of all solutions and dilutions.

**Standard Lead Solution.**—(a) Dissolve 0.1599 g.  $\text{Pb}(\text{NO}_3)_2$ , dried at  $110^\circ\text{C}$ ., in water with 10 ml. concentrated  $\text{HNO}_3$ , and dilute to 1000 ml. (b) Daily, dilute 10.00 ml. stock solution to 100 ml. to form a standard solution containing 0.010 mg. Pb per 1.00 ml. (c) Alternatively, prepare the standard solution by dissolving 0.1000 g. pure Pb metal in concentrated  $\text{HNO}_3$ , and diluting to the proper volumes. Prepare the standard solution daily.

**Stock Dithizone Solution.**—Dissolve 50 mg. diphenylthiocarbazone (dithizone) in 1 liter  $\text{CHCl}_3$ . Stopper tightly and store in the refrigerator. If necessary, purify the dithizone as described under "Cadmium," above.

**Standard Dithizone Solution.**—Dilute 100 ml. stock dithizone solution to 500 ml. with  $\text{CHCl}_3$ . Check daily for reliability, and store tightly stoppered in the refrigerator.

**Ammoniacal Citrate Solution.**—Dissolve 50 g. ammonium citrate in 100 ml. water, and adjust the pH to 8.5 to 9 with concentrated  $\text{NH}_4\text{OH}$ . Free the solution of heavy metal impurities by shaking with repeated 10-ml. portions stock dithizone solution until the final dithizone portion remains an unchanging green color. Then shake the solution with pure  $\text{CHCl}_3$  to extract the excess dithizone.

**Potassium Cyanide Solution, 50 g. KCN per 500 ml.**—Free the solution of heavy metal impurities by dithizone extraction as described for the ammoniacal citrate solution.

**Ammoniacal Cyanide Solution.**—Dissolve 40 g. KCN in 80 ml. water. Free the solution of heavy metal impurities by dithizone extraction as described for the ammoniacal citrate solution. Then add 1160 ml. concentrated  $\text{NH}_4\text{OH}$  to the extracted KCN solution, and dilute to 2 liters with water. Dispense this reagent with a safety pipet.

**Hydroxylamine Hydrochloride Solution, 20 g. per 100 ml.**

**Thymol Blue Indicator Solution, 0.1 g. per 100 ml.**

**Hydrochloric Acid, Concentrated.**

**Ammonium Hydroxide, Concentrated.**

**Nitric Acid, 1 + 99.**

**Sodium Sulfate.**

**Chloroform.**

**Procedure.**—If necessary, first remove interfering amounts of organic matter by the steps described in "General Procedure for Removal of Organic Matter Interference," under "Cadmium."

Select a sample volume containing 0.010 to 0.050 mg Pb. In the case of a potable water meeting USPHS drinking water standards for Pb take a minimum sample volume of 200 ml. Prepare a blank and a series of Pb standards (0.010, 0.020, 0.030, 0.040, and 0.050 mg) with sufficient water to give a total volume of 200 ml. Treat the blank and standards exactly as the sample throughout the procedure. Add 0.5 ml concentrated HCl and evaporate to 40 ml. Transfer with 10 ml water to a 125 ml separatory funnel. Shaking after each addition add 10 ml ammoniacal citrate solution, 2 ml  $\text{NH}_4\text{OH}$ , HCl solution, 10 drops thymol blue indicator, and enough concentrated  $\text{NH}_4\text{OH}$  to turn the indicator color to blue. Add 4 ml KCN solution and carefully adjust the pH to 8.5 to 9 with 1 + 99  $\text{HNO}_3$  signalled by the green color of the indicator. Extract the solution with 5 ml portions stock dithizone solution. Drain off each organic layer into another separatory funnel until the Pb is completely removed as evidenced by the unchanging green color of the final dithizone portion. Add 25 ml 1 + 99  $\text{HNO}_3$  to the combined extracts and shake vigorously for 1 min. to draw the Pb into the aqueous layer. Reject the  $\text{CHCl}_3$  layer. Treat the aqueous layer with 5 ml ammoniacal cyanide solution and exactly 20 ml standard dithizone solution. Shake for 1 min. and after the layers separate discard the first few milliliters of the organic layer. Rapidly determine the absorbance at 510 to 520  $\mu$  of the remaining clear  $\text{CHCl}_3$  layer from the sample and standards against pure  $\text{CHCl}_3$  or the reagent blank. If necessary remove any water droplets from the  $\text{CHCl}_3$  layer by filtrate through a small filter paper or a cotton or glass wool plug or a fritted glass funnel containing a 0.5 g layer of  $\text{Na}_2\text{SO}_4$ . When a  $\text{CHCl}_3$  reference is used correct the sample result by deducting the Pb content of the reagent blank carried through the entire procedure. For visual color matching place the colored organic layer in a dry 50 ml Nessler tube and compare the samples and standards by viewing transversely against a white background.

$$\text{Pb milligrams per liter} = \frac{A \times 1000}{\text{milliliters of sample}} \times \frac{B}{C}$$

where  $A$  = milligrams of Pb found photometrically or visually. The ratio  $B/C$  applies only when a large sample is digested for removal of organic interference the volume then made up to  $B$  and an aliquot  $C$  taken from it for color development.

### LITHIUM <sup>2</sup>

The entire section Flame Photometric Method under Sodium p 2478 below should be read carefully for the description of the bracketing method and other details pertinent to a successful flame photometric determination. Borosilicate glassware should be used for the storage of samples and standards because  $\text{LiCl}$  is occasionally used as a catalyst in the manufacture of polyethylene.

**Reagents** Standard Lithium Solution—(a) Weigh rapidly 0.6109 g  $\text{LiCl}$  dried overnight at 105°C to constant weight dissolve and dilute to 1000 ml with distilled water to form a stock solution containing 0.100 mg Li per 100 ml. (b) Dilute 20.00 ml stock solution to 1000 ml with distilled water to form a standard solution containing 2.0 mg per liter of Li.

**Sodium Sulfate Sodium Carbonate Solution**—Dissolve 5 g  $\text{Na}_2\text{SO}_4$  and 10 g  $\text{Na}_2\text{CO}_3$  and dilute to 1 liter with distilled water.

**Procedure**—Select a sample volume containing 0.0001 to 0.0015 mg Li and a Na and Mg concentration individually under 10 mg. Add 5.0 ml  $\text{Na}_2\text{SO}_4$ ,  $\text{Na}_2\text{CO}_3$



solution to the 50.0 ml. sample, and bring to a boil to coagulate the precipitate of  $\text{BaSO}_4$ ,  $\text{SrCO}_3$ ,  $\text{CaCO}_3$ , and possibly  $\text{MgCO}_3$ . Allow sufficient time for complete precipitation to avoid postprecipitation of  $\text{BaSO}_4$  following filtration. Remove the precipitate by means of a double-washed retentive filter paper, wash with distilled water, and dilute the filtrate to 50.0 ml. for the flame photometric measurement. Prepare a 1.8-mg. per liter Li standard by adding 5.0 ml.  $\text{Na}_2\text{SO}_4\text{-Na}_2\text{CO}_3$  solution to 50.0 ml. of the 2.0 mg. per liter Li standard solution. Make direct intensity measurements at wavelength 671  $\mu$ . Follow the manufacturer's instructions for the operation of the flame photometer at hand. Read the sample, distilled water (0 mg. per liter Li), and the Li standard as nearly simultaneously as possible; taking the average of several measurements on each solution. Prepare additional Li standards when distilled water and the 1.8 mg. per liter Li standard prove insufficient for calibration purposes. Alternatively, use the bracketing method of measurement.

$$\text{Li, milligrams per liter} = \frac{\text{milligrams of Li} \times 1000}{\text{milliliters of sample}}$$

### MAGNESIUM

The classical gravimetric method for Mg is acknowledged to yield the most reliable results. Generally a single precipitation of  $\text{MgNH}_4\text{PO}_4$  serves the purpose. Reprecipitation is resorted to only for the most exact work. The shorter photometric method is satisfactory for many potable waters. In routine practice, Mg is calculated by the difference secured from the complexometric titrations for hardness and Ca. This indirect approach is adequate for control purposes where interference presents no problem.

#### GRAVIMETRIC METHOD <sup>2,11</sup>

Suspended matter,  $\text{SiO}_2$ , Fe, Al, Mn, Ca, and Sr must be separated in advance of the Mg determination. Double precipitation is advisable for accurate work, in order to overcome the coprecipitation of various salts of Mg,  $\text{NH}_4$ ,  $\text{PO}_4$ , Cl, and oxalate, which is possible in the presence of a large excess of  $(\text{NH}_4)_2\text{HPO}_4$  and  $\text{NH}_4$  salts. An excess of  $\text{PO}_4$  and As may result in Mg losses through precipitation in the original water sample.

**Reagents.** Diammonium Hydrogen Phosphate Solution, 30 g. per 100 ml.

Methyl Red Indicator.

Ammonium Hydroxide, Concentrated.

Ammonium Hydroxide, 1 + 19.

Hydrochloric Acid, 1 + 1.

Hydrochloric Acid, 1 + 9.

Hydrochloric Acid, 1 + 99.

**Procedure.** Removal of Interference.—Remove the  $\text{SiO}_2$  and suspended matter as described in "Gravimetric Method," under "Silica," p. 2475, below. Next remove the Ca as described in "Oxalate Methods," under "Calcium," p. 2410, above.

Dilute or concentrate the filtrate from the Ca determination to a convenient volume.

**Precipitation of Magnesium.**—Select an aliquot containing less than 60 mg. Mg. Bring the total volume to 150 ml., and acidify with 1 + 1 HCl to the pink color of methyl red indicator. Add 10 ml.  $(\text{NH}_4)_2\text{HPO}_4$  solution, and cool in an ice water bath. Add concentrated  $\text{NH}_4\text{OH}$  dropwise, with constant stirring, until the

indicator color turns yellow. Continue stirring for 5 min then add 5 ml concentrated  $\text{NH}_4\text{OH}$  and stir vigorously for another 10 min. After allowing the covered solution to stand overnight in a cool place collect the precipitate on an ashless fine textured retentive filter paper and wash with cold 1 + 19  $\text{NH}_4\text{OH}$  discarding the filtrate and washings. If a single precipitation is adequate proceed to the paragraph entitled Gravimetric Finish below otherwise repeat the precipitation as follows.

**Reprecipitation of Magnesium**—Dissolve the precipitate by pouring onto the filter 50 ml warm 1 + 9  $\text{HCl}$  in small portions and then washing the filter paper thoroughly with hot 1 + 99  $\text{HCl}$ . After diluting to 125 to 150 ml add 1 to 2 ml  $(\text{NH}_4)_2\text{HPO}_4$  solution and cool the solution in an ice water bath. Reprecipitate the Mg by adding concentrated  $\text{NH}_4\text{OH}$  dry by drop with constant stirring until the methyl red indicator turns a yellow color. Add 5 ml concentrated  $\text{NH}_4\text{OH}$  and stir vigorously for 10 min. Allow the solution to stand overnight in a cool place.

**Gravimetric Finish**—Transfer the precipitate to an ashless fine textured retentive filter paper. Wash 5 to 8 times with 3 to 5 ml portions cold 1 + 19  $\text{NH}_4\text{OH}$  or until the washings become free from Cl. Carefully char the filter paper in a crucible that has previously been ignited and weighed. Burn off the final traces of paper without causing a flame and gradually increase the heat to  $1100^\circ\text{C}$  for 30 min or to constant weight. Cool the crucible in a desiccator and weigh the  $\text{Mg}_2\text{P}_2\text{O}_7$  residue.

$$\text{Mg milligrams per liter} = \frac{\text{milligrams of } \text{Mg}_2\text{P}_2\text{O}_7 \times 218.5}{\text{milliliters of sample}}$$

#### PHOTOMETRIC METHOD<sup>2, 3</sup>

Manganic and Zn ions must be absent. Iron in concentrations above 25 mg per liter augments the Mg color. Tolerable limits for other ions are 250 mg per liter Cl and 5 mg per liter for  $\text{PO}_4$  or F. Residual chlorine must be eliminated with  $\text{Na}_2\text{SO}_3$ .

**Reagents** **Standard Magnesium Solution**—Prepare the stock solution containing 100 mg Mg per 100 ml from the pure metal as described in (a) or from the salt as described in (b). (a) Place 1000 g metal in a 500 ml flask add 150 ml distilled water and 5 ml 1 + 1  $\text{H}_2\text{SO}_4$ . Apply the acid in 1 ml portions with thorough mixing and wait each time for the reaction to subside. Finally boil the solution gently for 10 min to dissolve the metal completely. Dilute the cooled solution to 1000 ml with distilled water. (b) Dissolve 10.136 g  $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$  in distilled water and dilute to 1000 ml. Determine the exact Mg concentration by the gravimetric method. (c) Dilute 100.0 ml stock solution to 1000 ml to form a standard solution containing 0.100 m, per 100 ml.

**Stabilizer Solution**—Place 10 g Colloresin 25 or Colloresin LV (products of Irwin Dyestuff Co. Montreal Quebec) or Methocel 25 (a product of Dow Chemical Co.) in a glass stoppered bottle containing 100 ml distilled water and shake a few times. Store in a refrigerator overnight to dissolve. Discard when mold growth or sediment appears.

**Brilliant Yellow Solution** 0.50 g per liter—Prepare every 2 or 3 days.

**Saturated Calcium Sulfate Solution**—Approximately 20 g per liter.

<sup>2</sup> Taras M. Anal. Chem. 20:1156, 1918.

Aluminum Sulfate Solution.—0.31 g.  $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$  per liter. Add 0.3 ml. concentrated  $\text{H}_2\text{SO}_4$ .

Sodium Sulfite Solution, 1.0 g. per 100 ml.—Prepare daily.

Sulfuric Acid, 0.02 *N*.

Sodium Hydroxide, 6 *N*.

**Procedure.**—Pipet into a 100-ml. volumetric flask a sample volume containing 0.1 to 0.8 mg. Mg, when Colloresin stabilizer is used, or 0.1 to 0.6 mg. Mg in the case of Methocel stabilizer. If necessary, reduce any residual chlorine with 1 ml.  $\text{Na}_2\text{SO}_3$  solution. Prepare the following calibration standards in 100-ml. volumetric flasks: 0, 0.100, 0.200, 0.400, and 0.600 or 0.800 mg. Mg. Treat the blank and standards exactly as the sample throughout the entire procedure. Add 1 ml. 0.02 *N*  $\text{H}_2\text{SO}_4$  (or sufficient acid to prevent the precipitation of the succeeding Ca and alum additions), 20 ml. saturated  $\text{CaSO}_4$  solution, and 5.0 ml. alum solution. Dilute to 80 ml. with distilled water, and mix. Add 5.0 ml. stabilizer solution, 2.0 ml. brilliant yellow solution, and 3.5 ml. 6 *N* NaOH. Dilute to 100 ml. with distilled water, mix, and within 5 to 60 min., read the absorbance at 525  $m\mu$  in a 1-cm. cell against the reagent blank.

$$\text{Mg, milligrams per liter} = \frac{\text{milligrams of Mg} \times 1000}{\text{milliliters of sample}}$$

#### MAGNESIUM BY CALCULATION

Determine the hardness and Ca values by means of the EDTA titrimetric methods, and convert the results into terms of  $\text{CaCO}_3$ . Calculate the Mg by the following equation:

$$\text{Mg, milligrams per liter} = 0.243(A - B)$$

where *A* = EDTA hardness expressed in terms of mg. per liter of  $\text{CaCO}_3$ ,

*B* = Ca hardness by EDTA titrimetric method expressed in terms of mg. per liter of  $\text{CaCO}_3$ .

#### MANGANESE <sup>2, 37</sup>

Chloride exceeding 60 mg. may interfere by formation of AgCl turbidity and by weakening the catalytic activity of Ag. A reasonable amount of organic matter and other reductants can be tolerated by prolonging the heating period and adding more  $(\text{NH}_4)_2\text{S}_2\text{O}_8$ . Undue boiling decomposes the excess  $(\text{NH}_4)_2\text{S}_2\text{O}_8$ , however, and brings about permanganate loss; an effect also caused by too slow cooling. A correction can be made by bleaching the permanganate color with  $\text{H}_2\text{O}_2$  when such colored ions as ferric, dichromate, Cu, and Ni interfere by absorbing light at 525  $m\mu$ .

Manganese should be determined immediately or the sample should be acidified with  $\text{HNO}_3$  at the time of collection to minimize adsorption or precipitation.

**Reagents.** Standard Manganese Solution.—(a) Compute by the following equation the volume of filtered and standardized 0.05 *N*  $\text{KMnO}_4$  titrant (preparation described under "Calcium," above, p. 2410) required to form a solution containing 0.050 mg. Mn per 1.00 ml.:

$$\text{KMnO}_4, \text{ milliliters} = \frac{4.55}{\text{normality of KMnO}_4}$$

<sup>37</sup> Nydahl, F., Anal. Chem. Acta, 3, 144, 1949.

Acidify this volume with 2 to 3 ml concentrated  $H_2SO_4$  and stirring constantly decolorize with the dropwise addition of  $NaHSO_3$  solution (10 g per 100 ml). Expel the excess  $SO_2$  by boiling then dilute the cooled solution to 1000 ml with distilled water. (b) Dilute 100.0 ml solution (a) to 1000 ml with distilled water to form a standard solution containing 0.005 mg Mn per 100 ml. Prepare daily.

**Acid Silver Mercuric Reagent**—Dissolve 75 g  $HgSO_4$  in 400 ml concentrated  $HNO_3$  and 200 ml distilled water. Add 200 ml 85%  $H_3PO_4$  and 0.035 g  $AgNO_3$  and dilute the cooled solution to 1 liter.

**Hydrogen Peroxide** 30%

**Ammonium Persulfate**

**Procedure**—Select a sample volume containing 0.005 to 0.1 mg Mn if estimations are to be made by visual color matching or less than 1.5 mg for absorbance measurements in a 1 cm cell. Pipet the sample into a flask or beaker add 5 ml acid silver mercuric reagent and evaporate or dilute to 90 ml. Prepare a series of visual standards with the following volumes of standard Mn solution (b) 0 10 20 40 80 120 160 and 200 ml. Alternatively prepare the photometric calibration curve from the following Mn standards 0 0.050 0.100 0.200 0.300 and 0.500 mg for readings in a 5 cm cell and 0 0.100 0.250 0.500 1.00 and 1.50 mg for a 1 cm cell. Dilute the blank and standards to 50.0 ml with distilled water add 5 ml acid silver mercuric reagent and treat exactly as the sample throughout the procedure. Add 1 g  $(NH_4)_2S_2O_8$  quickly bring to a boil and boil gently for 1 min to intensify the color development. Remove the heat source then 1 min later rapidly cool the solution under the tap. Dilute to 100 ml with distilled water mix and read the absorbance at  $525 m\mu$  or compare the colors visually in 100 ml tall form Nessler tubes. Correct for interfering color or turbidity by mixing the developed permanganate color in the cell with 1 drop 30%  $H_2O_2$  and repeating the absorbance measurement on the decolorized solution.

$$\text{Mn, milligrams per liter} = \frac{\text{milligrams of Mn} \times 1000}{\text{milliliters of sample}}$$

### METHANE <sup>25</sup>

The advantages of the combustible gas indicator method for  $CH_4$  are simplicity, speed and a sensitivity of 0.2  $m\%$  per liter of  $CH_4$ . Since ethane and vapors of combustible oils as well as  $CH_4$  may be determined by the combustible gas indicator this method enables an estimation of the total explosion hazard in the water supply. Hydrogen sulfide interference can be minimized by adding NaOH pellets to the container in advance of sampling.

The combustible gas indicator is available commercially under the following trade names: JW Combustible Gas Indicator, a product of Johnson Williams, Inc. Palo Alto Calif. Explosimeter, Methane Gas Detector and Methane Tester, products of Mine Safety Appliance Co. Pittsburgh Pa. and Vaportester, a product of Davis Emergency Equipment Co. Newark N. J.

**Reagent** Sodium Hydroxide

**Procedure** Preparation of Sampling Container—Prepare a 1 gal. glass bottle as illustrated in Fig. 487 fitting the 2 hole rubber stopper with an inlet tube extending to within 1 cm of the bottom and an outlet tube terminating about 1 cm above the stopper surface. Use metal or glass tubes and connect to the individual

<sup>25</sup> Rossum J. R., Villarruz P. A. and Wade J. A. J. Am. Water Works Assn. 42, 413 1950.

stopcocks, *A* and *B*, by means of 5-cm. lengths of rubber tubing and pinchcocks. Make sure that the entire assembly can maintain a low vacuum for several hours. Ascertain the volume of the assembly by filling with water and measuring the volume or weight of the water content.

**Collection of Sample.**—Operate the well for a long enough interval to secure a water from the desired aquifer. In order to insure a representative sample make certain that the well is equipped with a pump operating at sufficient submergence

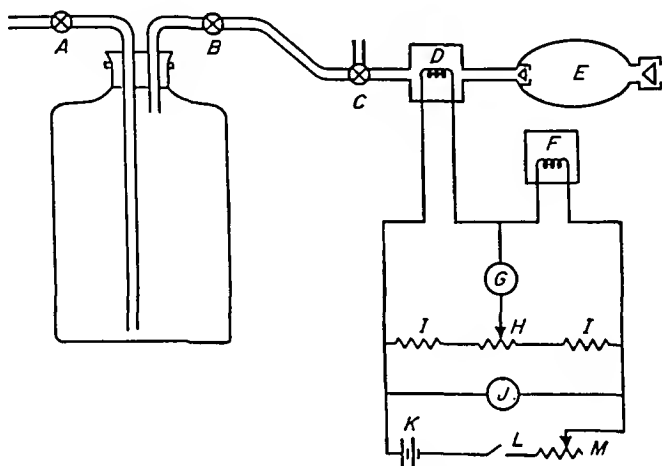


FIG. 48-7. Combustible Gas Indicator Circuit and Flow Diagram: *A* and *B*, 2-Way Stopcocks; *C*, 3-Way Stopcock; *D*, Active Filament (Exposed to Sample); *E*, Aspirator Bulb; *F*, Reference Filament (Shielded from Sample); *G*, Indicator Meter; *H*, Zero Adjusting Potentiometer; *I*, Fixed Resistor; *J*, Voltmeter; *K*, Battery; *L*, Switch; *M*, Volt Adjusting Rheostat. (Reproduced with permission from *Standard Methods for the Examination of Water and Wastewater*, 11th Ed., The American Public Health Assn., Inc., New York, 1960.)

and pressure to keep all of the gas dissolved, thereby preventing gas losses to the atmosphere.

**Preliminary Determination.**—Connect a rubber tube from the sampling tap to the inlet tube of the bottle and leave the outlet tube open. After filling the bottle half-full of water, close both inlet, *A*, and outlet, *B*, cocks, vigorously shake the bottle for 15 sec., and let the water stand for 1 min. Immediately zero the combustible gas indicator by opening the 3-way cock, *C*, to the air. By means of the suction bulb, *E*, draw gas from the outlet tube, at the same time leaving the inlet tube open to admit air. (Where facilities permit, substitute a laboratory filter pump for the suction bulb, and draw gas through the instrument at a rate of approximately 600 ml. per minute.) If the needle swings rapidly to a high level on the meter and then returns to zero, take a smaller volume of water for the final determination because the  $\text{CH}_4$ -air mixture is too rich to burn. If the needle deflection is too weak for an accurate reading, select a larger sample volume.

**Final Determination.**—In the presence of  $\text{H}_2\text{S}$  add 0.5 g.  $\text{NaOH}$  pellets to the empty bottle to suppress this gaseous interference. Evacuate the bottle by means of a filter pump. Connect a rubber tube from the sampling tap to the inlet tube of the bottle. Keep the outlet tube closed, and fill the bottle not more than three-quarters full with the sample. After the desired sample volume has been collected,

fill the bottle with air admitted through the inlet tube. Close the inlet cock and shake the bottle vigorously for 1 min. Allow the sample to stand a minimum of 2 hr. Zero the instrument by opening the 3 way cock to the air. Draw the gas from the bottle through the outlet tube, at the same time opening the inlet tube. Make the reading as swiftly as possible before the entering air dilutes the sample significantly. Measure the volume of the water sample.

Calculate the  $\text{CH}_4$  concentration by any of the following equations

$$\text{CH}_4 \text{ in sample, milligrams} = P \left( \frac{0.257V_g}{T} + \frac{890V_l}{H} \right)$$

where  $P$  = partial pressure of  $\text{CH}_4$  in millimeters of Hg,

$T$  = temperature in degrees Kelvin,

$V_g$  = milliliters of volume of gas phase,

$V_l$  = milliliters of volume of liquid phase, and

$H$  = Henry's law constant in millimeters of Hg per mole of  $\text{CH}_4$  per mole of water

The values for Henry's law constant are listed in Table 48-6<sup>39</sup>

TABLE 48-6 HENRY'S LAW CONSTANTS

Temperature, degrees C	Henry's Law Constant, H	Temperature, degrees C	Henry's Law Constant, H
0	$16.99 \times 10^6$	40	$39.46 \times 10^6$
5	$19.69 \times 10^6$	45	$41.83 \times 10^6$
10	$22.58 \times 10^6$	50	$43.85 \times 10^6$
15	$25.60 \times 10^6$	60	$47.57 \times 10^6$
20	$28.53 \times 10^6$	70	$50.62 \times 10^6$
25	$31.36 \times 10^6$	80	$51.84 \times 10^6$
30	$34.08 \times 10^6$	90	$52.60 \times 10^6$
35	$36.95 \times 10^6$	100	$53.30 \times 10^6$

When it is assumed that the determinations have been made at an atmospheric pressure of 760 mm and a temperature of 20°C, the following equation applies

$$\text{CH}_4, \text{ milligrams per liter} = Rf \left[ 6.7 \left( \frac{V_o - V_l}{V_l} \right) + 0.24 \right]$$

where  $R$  = instrument scale reading,

$V_o$  = milliliters of total volume of sample bottle,

$V_l$  = milliliters of volume of water sample, and

$f$  = factor dependent on the instrument used

When the instrument reads directly in percentage of  $\text{CH}_4$ ,  $f = 1.00$ . When the instrument reads in percentage of the lower explosive limit of  $\text{CH}_4$ ,  $f = 0.05$ . Some instruments require additional factors, which may be obtained from the instrument manufacturer. (One commercial instrument has a scale that reads in percentage of the lower explosive limit of combustible gases, and requires an additional factor of 0.77 for  $\text{CH}_4$ . Thus, the value of  $f = 0.77 \times 0.05 = 0.0385$ .)

<sup>39</sup> Reproduced with permission from Standard Methods for the Examination of Water and Wastewater, 11th Ed., The American Public Health Assn., Inc., New York, 1960.

The following equation should be used when the temperature and barometric pressure deviate significantly from the normals of 20°C. and 760 mm:

$$\text{CH}_4, \text{ milligrams per liter} = RBf \left[ 2.57 \left( \frac{V_o - V_i}{TV_i} \right) + \frac{8900}{H} \right]$$

where the additional symbol  $B$  = barometric pressure in millimeters of Hg.

### NITRATE

The phenoldisulfonic acid method can be applied to the determination of  $\text{NO}_3$  over a fairly wide range, and particularly to the small amounts below 1 mg. of nitrogen per liter characteristic of many potable waters. However, the majority of samples entail the removal of interfering concentrations of chloride. The brucine method, on the other hand, is free of chloride interference and finds principal application in the 1 to 10 mg. per liter nitrate N range.

#### *PHENOLDISULFONIC ACID METHOD*<sup>2,40</sup>

The phenoldisulfonic acid method is suitable for determinations in the range 0.01 to 2 mg. per liter nitrate N at 410  $m\mu$  and up to 12 mg. per liter at 480  $m\mu$ . Chloride seriously interferes and must be reduced to a minimum (preferably below 10 mg. per liter) in the sample, otherwise low  $\text{NO}_3$  values will result. Nitrite N levels below 0.2 mg. per liter can be tolerated, but in excess of 0.2 mg. per liter, nitrite N must be compensated for by quantitative oxidation to  $\text{NO}_3$ , and subsequent deduction from the final  $\text{NO}_3$  value. Colored ions and materials that physically affect the color system must also be absent.

The visual standards prepared from the best reagents are normally stable for 2 to 4 weeks. Continued color development in the visual standards after several hours' standing is characteristic of a phenoldisulfonic acid reagent that contains considerable initial color. In such an event, frequent preparation of each series of visual standards is mandatory.

**Reagents.** Stock Nitrate Solution.—Dissolve 0.7218 g.  $\text{KNO}_3$ , dried at 105°C., in distilled water and dilute to 1000 ml. to form a solution containing 0.100 mg. N per 1.00 ml.

Standard Nitrate Solution.—Evaporate 50.00 ml. stock  $\text{NO}_3$  solution to dryness on a steam or water bath, dissolve the residue in 2 ml. phenoldisulfonic acid reagent by rubbing with a glass rod, and dilute to 500 ml. with distilled water to form a solution containing 0.010 mg. N per 1.00 ml.

Phenoldisulfonic Acid Reagent.—Dissolve 25 g. pure white phenol in 150 ml. concentrated  $\text{H}_2\text{SO}_4$ , add 75 ml. fuming  $\text{H}_2\text{SO}_4$  (15% free  $\text{SO}_3$ ), mix thoroughly, and heat for 2 hr. on a hot water bath. If desired, substitute 170 ml. concentrated  $\text{H}_2\text{SO}_4$  and 55 ml. fuming  $\text{H}_2\text{SO}_4$  (20% free  $\text{SO}_3$ ).

Standard Silver Sulfate Solution.—Dissolve 4.397 g.  $\text{Ag}_2\text{SO}_4$ ,  $\text{NO}_3$ -free, in distilled water, and dilute to 1000 ml. to form a solution equivalent to 1.0 mg. Cl per 1.00 ml. Standardize by diluting 25.00 or 50.00 ml. standard 0.0141  $N$   $\text{NaCl}$  to 100 ml. with deionized distilled water or redistilled water, adding 1.0 ml.  $\text{K}_2\text{CrO}_4$  indicator, and titrating as described in "Chloride," above, p. 2414. Store in a brown bottle or in the dark.

EDTA Reagent.—Form a thoroughly wetted paste by rubbing 50 g. disodium ethylenediaminetetraacetate dihydrate and 20 ml. distilled water with a glass rod.

<sup>40</sup> Taras, M. J., *Anal. Chem.*, **22**, 1020, 1950.

Add 60 ml concentrated  $\text{NH}_4\text{OH}$  and mix until the paste dissolves (Alternately use the EDTA solution described under Ammonia Nitrogen )

Ammonium Hydroxide, Concentrated

Sodium Hydroxide, 1 N

Sulfuric Acid 1 N

Reagents for Treatment of Unusual Interference Hydrogen Peroxide Solution—Dilute 10 ml 30%  $\text{H}_2\text{O}_2$  (low in  $\text{NO}_3$ ) to 100 ml with distilled water

Aluminum Hydroxide Suspension

Zinc Sulfate Solution

Sodium Hydroxide 15 N

Sulfuric Acid 1 N

Potassium Permanganate 0.1 N

Procedure Removal of Color and Turbidity—Apply 45 ml well shaken  $\text{Al}(\text{OH})_3$  suspension to 150 ml sample stir and allow the floc to settle several times Then filter and discard the initial 25 ml filtrate

Alternately coagulate the sample with  $\text{ZnSO}_4$  solution and 15 N NaOH as described under Ammonia Nitrogen p 2449 below but omit the use of EDTA or Rochelle salt

Treatment of Nitrite Interference—Determine the  $\text{NO}_2$  concentration as described under Nitrite below If the nitrite N concentration exceeds 0.2 mg per liter acidify a 100 ml sample with 1 ml 1 N  $\text{H}_2\text{SO}_4$  Add drop by drop with constant stirring either 0.1 N  $\text{KMnO}_4$  or  $\text{H}_2\text{O}_2$  solution and allow the sample to stand 15 min for complete conversion of the  $\text{NO}_2$  to  $\text{NO}_3$  (Sufficient  $\text{KMnO}_4$  is indicated by the persistence of a faint pink color throughout the 15 min period) Enter the proper NO deduction at the end of the  $\text{NO}_3$  determination

Removal of Chloride Determine the Cl concentration as described under Chloride above and treat a 100 ml sample with an equivalent (not an excess) amount of standard  $\text{Ag}_2\text{SO}_4$  solution For best results allow the covered precipitate to settle overnight at laboratory temperature away from strong light If necessary and only as a last resort coagulate the  $\text{AgCl}$  by heat Centrifuge or filter off the precipitate

Preparation of Visual Comparison Standards—Measure the following volumes of standard  $\text{NO}_3$  solution into 50 ml Nessler tubes 0 0.10 0.30 0.50 0.70 1.0 1.5 2.0 3.5 6.0 10 15 20 and 30 ml If desired use 100 ml Nessler tubes and double the volumes of standard  $\text{NO}_3$  solution Add 2.0 ml phenoldisulfonic acid reagent and 7 ml concentrated  $\text{NH}_4\text{OH}$

Color Development—Neutralize the clear and colorless sample to pH 7 to 8.5 with 1 N NaOH or 1 N  $\text{H}_2\text{SO}_4$  Pipet a sample volume containing less than 0.2 mg nitrite N into a casserole or beaker and evaporate to dryness over a steam or water bath

Prepare a blank and a series of calibration standards in the range 0.030 to 0.200 mg nitrite N for absorbance readings at 410 m $\mu$  in a 1 cm cell and 0.005 to 0.050 mg N for a 5 cm cell Add 2.0 ml phenoldisulfonic acid reagent and 7 ml concentrated  $\text{NH}_4\text{OH}$  to the blank and each standard

Dissolve the sample residue with 2.0 ml phenoldisulfonic acid reagent by rubbing with a glass rod If necessary and only as a last resort heat gently on the hot water bath a short time to dissolve a resistant residue but avoid charring the residue Dilute with 20 ml distilled water and add sufficient concentrated  $\text{NH}_4\text{OH}$  (approximately 7 ml) to develop the maximum yellow color Filter off any resulting flocculant hydroxides or add EDTA reagent drop by drop with stirring



until the  $\text{Mg}(\text{OH})_2$  and  $\text{Ca}(\text{OH})_2$  redissolve. Transfer the clear solution or filtrate to a 50- or 100-ml. Nessler tube or volumetric flask. Add the distilled water washings of the casserole, beaker, or filter to the Nessler tube or volumetric flask, dilute to the mark, and mix. Measure the absorbance or visually match the colors.

$$\text{Nitrate N, milligrams per liter} = \frac{\text{milligrams of nitrate N} \times 1000}{\text{milliliters of sample}}$$

$$\text{NO}_3, \text{ milligrams per liter} = \text{milligrams per liter nitrate N} \times 4.43$$

#### BRUCINE METHOD <sup>2, 11, 41</sup>

All strong oxidants and reductants interfere in the brucine method. Oxidants can be demonstrated by the yellow color produced with the *o*-tolidine reagent described under "Residual Chlorine," p. 2416, above. Sodium arsenite satisfactorily dechlorinates residual chlorine concentrations up to 5 mg. per liter, and may be used in slight excess without deleterious effect. A slight positive interference results from the presence of ferrous, ferric, and manganic ions, but the interference is negligible at levels below 1 mg. per liter. Chloride and nitrite do not interfere in the specified procedure. Colored ions and materials that physically affect the color system must be absent.

**Reagents.** Standard Nitrate Solution.—Dilute 100.0 ml. stock  $\text{NO}_3$  solution (0.7218 g.  $\text{KNO}_3$  per 1000 ml.) to 1000 ml. with distilled water to form a standard solution containing 0.010 mg. N per 1.00 ml.

**Brucine-Sulfanilic Acid Reagent.**—Dissolve 1 g. brucine sulfate and 0.1 g. sulfanilic acid (also called 4-aminobenzenesulfonic acid) in 70 ml. hot distilled water, add 3 ml. concentrated  $\text{HCl}$ , cool the solution to room temperature, and dilute to 100 ml. The reagent retains its effectiveness for several months despite the gradual appearance of a pink color. Dispense this reagent with a safety pipet.

**Sulfuric Acid Solution.**—Carefully add 500 ml. concentrated  $\text{H}_2\text{SO}_4$  to 75 ml. distilled water. Keep tightly stoppered to protect against atmospheric moisture.

**Sodium Arsenite Solution, 0.028 N, 1.83 g.  $\text{NaAsO}_2$  per liter.**

**Procedure.**—If necessary, dechlorinate a 50-ml. sample by adding 0.1 ml.  $\text{NaAsO}_2$  solution for each 0.05 mg. residual chlorine, plus 1 drop in excess.

If necessary, dilute the sample with distilled water to bring the nitrate N concentration within the 1 to 10 mg. per liter range.

Prepare a series of  $\text{NO}_3$  standards (0.050, 0.150, 0.250, 0.350, 0.500, 0.750, and 1.00 mg. N) in 100-ml. volume with distilled water.

Pipet a 2-ml. aliquot of the sample and each standard solution into a 50-ml. beaker. Treat the blank and calibration standards exactly as the sample throughout the procedure. Add 1.0 ml. brucine-sulfanilic acid reagent. Introduce 10 ml.  $\text{H}_2\text{SO}_4$  solution into a second and similar 50-ml. beaker. Then carefully pour the brucine-treated contents of the first beaker into the companion beaker containing the  $\text{H}_2\text{SO}_4$ . Repeat the transfer from one beaker to the other 4 to 6 times to insure thorough mixing. Allow the color to develop in the dark for  $10 \pm 1$  min. (cover the beakers with a cardboard carton if convenient). During the 10-min. interim, place 10 ml. distilled water in each of the empty beakers. Add this water to the treated solutions, and mix as before. Cool the beakers in the dark for an

<sup>41</sup> Greenberg, A. E., Rossum, J. R., Villarruz, P. A., and Moskowitz, N., J. Am. Water Works Assn., 50, 821, 1958.

additional 20 to 30 min. Read the absorbance at 410  $m\mu$  in a cell of 1 cm length or longer using the blank as the reference

$$\text{Nitrate N milligrams per liter} = \frac{\text{milligrams of nitrate N} \times 1000}{\text{milliliters of sample}}$$

$$\text{NO}_3 \text{ milligrams per liter} = \text{milligrams per liter of nitrate N} \times 4.43$$

### NITRITE 11 42

Interferences fall into 4 classes (a) amines and strong oxidants and reductants that destroy nitrite (b) ions that precipitate under the reaction conditions (c) ions that upset the optimum acidity and (d) colored ions that physically disturb the color system. The following ions should be absent: ferric, mercurous, nitrous, auric, chloroplatinate, metavanadate, Ag and Bi. High  $\text{NH}_3$  concentrations should be avoided. Iodide should be limited to 0.1 mg and Cu to 0.05 mg in the sample portion. Nitrogen trichloride imparts a false red color, so a check for a free available chlorine and  $\text{NCl}_3$  residual is advisable by the procedure described in Orthotolidine Arsenite (OTA) Method, p 2416 under Residual Chlorine. The addition of 0.5 ml disodium ethylenediaminetetraacetate dihydrate (0.5 g per 100 ml) to the untreated sample prevents Fe interference.

The sample should be collected in a bacteriologically sterile bottle and the determination undertaken with dispatch to prevent bacterial oxidation or reduction.

**Reagents.** Nitrite Free Water.—Prepare  $\text{NO}_2$  free water by either of the following methods: (a) Add a crystal each of  $\text{KMnO}_4$  and  $\text{Br}(\text{OH})_2$  or  $\text{Ca}(\text{OH})_2$  (or 1 to 2 drops of alkaline  $\text{KMnO}_4$  reagent described under Albuminoid Nitrogen, p 2453 below) to 1 liter distilled water and redistill in an all borosilicate glass apparatus. Reject the initial 50 ml distillate and collect that portion that is free of permanganate. Use the o-tolidine reagent described in Orthotolidine Arsenite (OTA) Method, p 2416 under Residual Chlorine to test for the presence (appearance of yellow color) of permanganate. (b) To 1 liter distilled water add 1 ml concentrated  $\text{H}_2\text{SO}_4$ , 0.2 ml  $\text{MnSO}_4$  solution (preparation described under Dissolved Oxygen, p 2458 below) and sufficient 0.1 N  $\text{KMnO}_4$  (1 to 3 ml) to confer a permanent pink color. After 15 min decolorize carefully with  $(\text{NH}_4)_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$  solution (0.9 g per liter).

**Standard Nitrite Solution.**—(a) Dissolve 1.232 g  $\text{NaNO}_2$  in distilled water and dilute to 1000 ml to form a stock solution containing approximately 250 mg per liter of nitrite N. Standardize the stock solution as follows: pipet 50 ml standard 0.007 N  $\text{KMnO}_4$  (prepared and standardized as described under Calcium, p 2410 above), 1 ml concentrated  $\text{H}_2\text{SO}_4$  and 50.00 ml  $\text{NaNO}_2$  solution into a glass stoppered bottle. Shake the stoppered flask frequently and introduce 2 g KI after 15 min of reaction time. Titrate with standard 0.025 N  $\text{Na}_2\text{S}_2\text{O}_3$  (prepared and standardized as described under Dissolved Oxygen, p 2457 below) to the first disappearance of the blue starch indicator color.

$$\text{Nitrite N milligrams per liter} = \frac{[(A \times B) - (C \times D)] \times 7000}{\text{milliliters of NaNO}_2 \text{ taken for titration}}$$

where  $A$  = milliliters of standard  $\text{KMnO}_4$  solution used,

$B$  = normality of standard  $\text{KMnO}_4$  solution,

$C$  = milliliters of standard  $\text{Na}_2\text{S}_2\text{O}_3$  titration and

$D$  = normality of standard  $\text{Na}_2\text{S}_2\text{O}_3$  titrant

Preserve the stock solution with 1 ml.  $\text{CHCl}_3$ . (b) Dilute to 250 ml. the calculated volume (approximately 50 ml.) of the stock  $\text{NaNO}_2$  solution with  $\text{NO}_2$ -free water to form an intermediate dilution containing 50.0 mg. per 1000 ml. nitrite N. Preserve this solution with 1 ml.  $\text{CHCl}_3$ . (c) Dilute 10.00 ml. solution (b) to 1000 ml. with  $\text{NO}_2$ -free water to form a standard solution containing 0.0005 mg. N per 1.00 ml. Prepare the standard solution daily.

**Sulfanilic Acid Reagent.**—Dissolve 0.60 g. 4-aminobenzenesulfonic acid in 70 ml. hot, distilled water. Cool the solution to room temperature, add 20 ml. concentrated  $\text{HCl}$ , and dilute to 100 ml. with distilled water.

**1-Naphthylamine Hydrochloride Reagent.**—Dissolve 0.60 g. 1-naphthylamine hydrochloride in distilled water containing 1 ml. concentrated  $\text{HCl}$ , and dilute to 100 ml. Filter if necessary, and store in a refrigerator to prolong the useful life of the reagent.

**Sodium Acetate Solution, 2 M.**—16.4 g.  $\text{NaC}_2\text{H}_3\text{O}_2$  or 27.2 g.  $\text{NaC}_2\text{H}_3\text{O}_2 \cdot 3\text{H}_2\text{O}$  per 100 ml.

**Aluminum Hydroxide Suspension.**

**Zinc Sulfate Solution.**

**Sodium Hydroxide, 15 N.**

**Sodium Hydroxide, 1 N.**

**Hydrochloric Acid, 1 N.**

**Procedure. Removal of Color and Turbidity.**—If necessary, clarify the sample by centrifuging.

When an interfering amount of color and turbidity is present, apply 3 ml. well-shaken  $\text{Al}(\text{OH})_3$  suspension to each 100 ml. sample, stir, and allow the floc to settle several times. Then filter and discard the initial 25 ml. filtrate.

Alternatively, coagulate the sample with  $\text{ZnSO}_4$  solution and 15 N  $\text{NaOH}$  as described in "Treatment of Turbid or Colored Sample for Direct Nesslerization," p. 2451, below, under "Ammonia Nitrogen," but omit the use of EDTA or Rochelle salt.

**Color Development.**—Pipet a sample volume containing 0.00005 to 0.0012 mg. nitrite N into a 50-ml., tall-form Nessler tube or volumetric flask. Neutralize the sample to pH 7 with 1 N  $\text{NaOH}$  or 1 N  $\text{HCl}$ . Prepare a blank and a series of nitrite standards in the range 0.00025 to 0.0025 mg. N for absorbance measurements in a 5-cm. cell; or a series of visual comparison standards from the following volumes of standard nitrite solution (c): 0, 0.10, 0.20, 0.40, 0.70, 1.0, 1.4, 1.7, 2.0, and 2.5 ml. Dilute the blank, standards, and sample to 50.0 ml.; mix, and add 1.00 ml. sulfanilic acid reagent. (At this point the pH of the mixed solution should be about 1.4.) Within 3 to 10 min., add 1.0 ml. 1-naphthylamine hydrochloride reagent and 1.0 ml.  $\text{NaC}_2\text{H}_3\text{O}_2$  solution. (At this stage the pH of the mixed solution should be 2.0 to 2.5.) Read the absorbance at 520  $\text{m}\mu$  or visually match the colors within 10 to 30 min.

$$\text{Nitrite N, milligrams per liter} = \frac{\text{milligrams of nitrite N} \times 1000}{\text{milliliters of sample}}$$

$$\text{NO}_2, \text{ milligrams per liter} = \text{milligrams per liter of nitrite N} \times 3.29$$

### AMMONIA NITROGEN <sup>2,11</sup>

The distillation, Nesslerization, and titration steps in the  $\text{NH}_3$  determination can be varied to suit the situation or convenience of the analyst. Direct Nessler-

ization can be practiced routinely on a familiar water supply free of interference and bearing  $\text{NH}_3$  levels in excess of 0.1 mg per liter

Distillation for the most part overcomes the common interferences and enables the determination of trace amounts of  $\text{NH}_3$ . Unfamiliar samples should be distilled for reliable results. High Ca concentrations require an increased volume of  $\text{PO}_4$  buffer and preliminary pH adjustment of the sample to override the precipitation that occurs during distillation. Sulfide should be precipitated in the distilling flask with a little  $\text{PbCO}_3$ . Volatile substances such as formaldehyde and related aldehydes, acetone, alcohols, and other undefined organic bodies may be boiled off prior to distillation. However, urea hydrolyzes on distillation at pH 7.4 leading to erroneous high  $\text{NH}_3$  values.

*Interference in the Nesslerization reaction takes 2 guises: the formation of an off color and the formation of turbidity.* Hydrazine, glycine, and a number of aliphatic and aromatic amines and organic chloramines individually produce yellowish and greenish off colors or a turbidity with Nessler reagent.<sup>43</sup> A titrimetric finish can be employed when neutral organic bodies appear in the distillate. But the presence of volatile amines in the distillate will lead to excessive  $\text{NH}_3$  results by the titration method. Care should be exercised at all times to avoid contamination of the sample solutions and the apparatus by  $\text{NH}_3$  fumes derived from other laboratory operations.

A judicious combination of wavelength and light path enables the photometric estimation of  $\text{NH}_3$  over a considerable range. The calibration curve should be prepared under conditions identical to those for the sample.

Although promptness in analysis is desirable, microbiological activity can be repressed somewhat by refrigerating the sample or by the addition of 0.8 ml concentrated  $\text{H}_2\text{SO}_4$  to each liter of sample. The acidified sample must be neutralized with  $\text{NaOH}$  or  $\text{KOH}$  as the first step in the procedure. Residual chlorine should also be reduced immediately after the sample is collected to arrest the consumption of  $\text{NH}_3$ .

**Reagents: Deionized Distilled Water**—This should be used in the preparation of all solutions and dilutions.

**Phosphate Buffer Solution, pH 7.4**—Dissolve 14.3 g  $\text{KH}_2\text{PO}_4$  and 68.8 g  $\text{K}_2\text{HPO}_4$  and dilute to 1 liter with water.

**Boric Acid Absorbant** 20 g  $\text{H}_3\text{BO}_3$  per liter

**Sodium Thiosulfate Dechlorinating Solution** 3.5 g  $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$  per liter

**Sodium Hydroxide** 1 N

**Sulfuric Acid** 1 N

**Reagents for Nesslerization** **Standard Ammonium Chloride Solution**—(a) Dissolve 3.819 g  $\text{NH}_4\text{Cl}$  dried at 100°C and dilute to 1000 ml with water. (b) Dilute 10.00 ml stock solution to 1000 ml with water to form a standard solution containing 0.010 mg N or 0.0122 mg  $\text{NH}_3$  per 100 ml.

**Nessler Reagent**—Dissolve 100 g  $\text{HgI}_2$  and 70 g  $\text{KI}$  in a small volume of water. Dissolve 160 g  $\text{NaOH}$  in 500 ml water. Combine the 2 solutions and dilute to 1 liter. Use only the supernatant liquid for Nesslerization at all times.

**Zinc Sulfate Solution** 100 g  $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$  per liter

**EDTA Solution**—Dissolve 50 g disodium ethylenediaminetetraacetate dihydrate in 60 ml water containing 10 g  $\text{NaOH}$ . Warm to dissolve, cool to room temperature, and dilute to 100 ml.

<sup>43</sup> Taras, M. J. J. Am. Water Works Assn. 45:47, 1953.

**Rochelle Salt Solution.**—Dissolve 50 g.  $\text{KNaC}_4\text{H}_4\text{O}_6 \cdot 4\text{H}_2\text{O}$  in 100 ml. water, boil off 30 ml. solution, and dilute to 100 ml.

**Sodium Hydroxide, 15 N.**

**Reagents for Permanent Color Standards. Potassium Chloroplatinate Solution.**—Dissolve 2.0 g.  $\text{K}_2\text{PtCl}_6$  in 500 ml. distilled water containing 100 ml. concentrated  $\text{HCl}$ , and dilute to 1 liter.

**Cobaltous Chloride Solution.**—Dissolve 12.0 g.  $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$  in 300 ml. distilled water containing 100 ml. concentrated  $\text{HCl}$ , and dilute to 1 liter.

**Reagents for Titrimetric Finish. Standard Acid Titrant, 0.02 N.**—Dilute 200 ml. 0.1 N  $\text{HCl}$  or  $\text{H}_2\text{SO}_4$  to 1 liter with water. Standardize against standard 0.0200 N  $\text{Na}_2\text{CO}_3$  (preparation described under "Alkalinity," p. 2400, above) under exactly the same conditions (similar volumes of final solution and indicator solution) as for the titration of the distillates. Pipet a volume of standard 0.0200 N  $\text{Na}_2\text{CO}_3$  that approximates either the average or median (whichever is applicable) titration prevailing in the distillates encountered in the particular laboratory. The equivalence of 0.0200 N acid is 0.28 mg. N per 1.00 ml.

**Mixed Indicator Solutions.**—Either solution (a) or (b) is satisfactory. (a) *Mixed Methylene Blue-Methyl Red Indicator Solution.*—Separately dissolve 0.133 g. methyl red and 0.067 g. methylene blue in minimal volumes of 95% ethyl or isopropyl alcohol, then combine the 2 solutions and dilute to 100 ml. with the alcohol. Prepare monthly. (b) *Mixed Bromcresol Green-Methyl Red Indicator Solution.*—Prepare as described in "Alkalinity," above.

**Procedure. Distillation.**<sup>44</sup>—Select a sample volume containing up to 1.0 mg.  $\text{NH}_3$  nitrogen if the distillate is to be Nesslerized or 0.5 to 5 mg. N for a titrimetric finish. Steam out the borosilicate-glass distillation apparatus illustrated in Fig. 48-6 (p. 2432) by boiling water in the flask until the distillate becomes  $\text{NH}_3$ -free, as demonstrated with Nessler reagent.

Although a 500-ml. sample, or an aliquot diluted to 500 ml., will suffice for most purposes, take a sample of 700 to 1000 ml. if the  $\text{NH}_3$  nitrogen falls below 0.05 mg. per liter or an albuminoid N determination is to be performed on the same sample. Dechlorinate the residual chlorine with the exactly equivalent amount of  $\text{Na}_2\text{S}_2\text{O}_3$  solution. If the sample is acid or alkaline, neutralize to pH 7 with 1 N  $\text{NaOH}$  or 1 N  $\text{H}_2\text{SO}_4$ , using a pH meter. Add 10 ml. or more phosphate buffer solution, to maintain the sample pH at  $7.4 \pm 0.2$  throughout the distillation. For samples containing more than 250 mg. per liter of Ca, first add up to 40 ml. phosphate buffer solution, and then adjust the pH to 7.4 with 1 N  $\text{NaOH}$  or 1 N  $\text{H}_2\text{SO}_4$ . Transfer the dechlorinated, neutralized, and buffered sample to the 1-liter or 2-liter distilling flask, stopper, and distill. Collect the distillate in a 50-ml. Nessler tube, when the  $\text{NH}_3$  nitrogen is less than 0.01 mg., or a 200-ml. volumetric flask, when the  $\text{NH}_3$  nitrogen is between 0.01 and 0.05 mg. Collect 300 ml. distillate below the surface of 50 ml.  $\text{H}_3\text{BO}_3$  absorbant when the  $\text{NH}_3$  nitrogen falls in the range of 0.05 to 1.0 mg. Use an additional 50 ml.  $\text{H}_3\text{BO}_3$  for every additional 1 mg.  $\text{NH}_3$  nitrogen. Cleanse the condenser by lowering the distillate out of contact with the delivery tube during the last 1 or 2 min. of distillation.

**Treatment of Turbid or Colored Sample for Direct Nesslerization.**—Mixing after each addition, treat a 100-ml. sample with 1 ml.  $\text{ZnSO}_4$  solution and 0.3 ml. 15 N  $\text{NaOH}$  to raise the pH to 10.5 as determined by a pH meter and a high-pH glass electrode. Allow the floc to settle. Clarify by centrifuging or filtering through

<sup>44</sup> Nichols, M. S., and Foote, M. E., *Ind. Eng. Chem., Anal. Ed.*, 3, 311, 1931.

filter paper. Discard the first 25 ml filtrate if resort is made to filter paper. Add 1 drop EDTA solution or 1 or 2 drops of Rochelle salt solution to prevent calcium or magnesium hydroxide turbidity upon Nesslerization.

**Nesslerization**—Select a distillate aliquot or a volume of clear sample containing  $\text{NH}_3$  nitrogen in accordance with the following measurement requirements for the visual color matching method— $\text{NH}_3$  nitrogen concentrations up to 0.060 mg for photometric measurements in a 5 cm cell and the wavelength range of 400 to 425  $\text{m}\mu$ —0.005 to 0.060 mg N for photometric measurements in a 1 cm cell and the wavelength range of 400 to 425  $\text{m}\mu$ —0.020 to 0.250 mg N, and for photometric measurements in a 1 cm cell and the wavelength range of 450 to 500  $\text{m}\mu$ —up to 0.500 mg N.

Transfer 50.0 ml distillate or clear sample or an aliquot diluted to 50.0 ml into a Nessler tube and bring to room temperature. Add 1.0 ml Nessler reagent and mix adequately by inverting the tube at least 6 times. Measure the color photometrically or visually after exactly 10 min if the  $\text{NH}_3$  nitrogen is above 0.01 mg and after exactly 30 min, if below 0.01 mg N. Use an identical reaction period and temperature for the Nesslerized blank and  $\text{NH}_3$  nitrogen standards as for the sample.

TABLE 48-7 PERMANENT COLOR STANDARDS FOR VISUAL  $\text{NH}_3$  ESTIMATION

Ammonia Nitrogen Equivalent in 50 ml Volume mg	Approximate Volume of $\text{K}_2\text{PtCl}_6$ Solution ml	Approximate Volume of $\text{CoCl}_2$ Solution ml
0.000	1.2	0.0
0.002	2.8	0.0
0.004	4.7	0.1
0.007	5.9	0.2
0.010	7.7	0.5
0.014	9.9	1.1
0.017	11.4	1.7
0.020	12.7	2.2
0.025	15.0	3.3
0.030	17.3	4.5
0.035	19.0	5.7
0.040	19.7	7.1
0.045	19.9	8.7
0.050	20.0	10.4
0.060	20.0	15.0

Prepare the appropriate permanent standards in 50 ml Nessler tubes by diluting the volumes of  $\text{K}_2\text{PtCl}_6$  and  $\text{CoCl}_2$  solutions specified in Table 48.7<sup>45</sup>. Modify and adjust the tints of these permanent standards as necessary by checking with

<sup>45</sup> Reproduced with permission from Standard Methods for the Examination of Water and Wastewater 11th Ed. The American Public Health Assn. New York 1960.

Nesslerized  $\text{NH}_4\text{Cl}$  standard solutions. Recheck and readjust the permanent standards every time a new batch of Nessler reagent is prepared.

For best results prepare the photometric calibration curve by carrying known  $\text{NH}_4\text{Cl}$  standard solutions through all of the procedural steps including distillation if used for water samples.

**Titration.**—To the flask containing the distillate, add 3 to 5 drops mixed indicator, and titrate with 0.02 *N* standard acid to the color of the color comparison standard prepared from the same number of drops of mixed indicator, the same volume of  $\text{H}_3\text{BO}_3$  absorbant, and the same total volume of solution as the titrated distillate.

**Reagent Blank.**—Correct the sample result by deducting the  $\text{NH}_3$  nitrogen content of the reagent blank carried through all of the steps of the procedure used.

$$\text{NH}_3 \text{ nitrogen, milligrams per liter} = \frac{A \times 1000}{\text{milliliters of sample}} \times \frac{B}{C}$$

where *A* = milligrams of  $\text{NH}_3$  nitrogen found colorimetrically or titrimetrically. The ratio *B/C* applies only when a sample is distilled, the volume then made up to *B*, and aliquot *C* taken from it for color development or titration.

$\text{NH}_3$ , milligrams per liter = milligrams per liter of  $\text{NH}_3$  nitrogen  $\times$  1.216.

$\text{NH}_4$ , milligrams per liter = milligrams per liter of  $\text{NH}_3$  nitrogen  $\times$  1.288.

#### ALBUMINOID NITROGEN<sup>2, 46</sup>

The albuminoid N determination is normally performed on the same sample used for the distillation of  $\text{NH}_3$  nitrogen. Therefore, the entire discussion on "Ammonia Nitrogen," above, should be read and understood before the albuminoid N determination is attempted. The same precautions as in "Ammonia Nitrogen," apply to promptness of examination, sample refrigeration or preservation, and the importance of guarding against outside  $\text{NH}_3$  contamination.

**Reagents.** Deionized Distilled Water.—This should be used for the preparation of all solutions and dilutions.

**Appropriate Reagents Described Under "Ammonia Nitrogen."**

**Alkaline Potassium Permanganate Reagent.**—In a 3-l., borosilicate-glass beaker, dissolve 16 g.  $\text{KMnO}_4$  in a minimum volume of water. Add 288 g.  $\text{NaOH}$  or 404 g.  $\text{KOH}$ , and sufficient water to make up to 2.5 l. Concentrate to 2 l. on an electric hot plate.

**Procedure.**—Select a sample volume, containing up to 1.0 mg. albuminoid N, if the distillate is to be Nesslerized, or 0.5 to 5 mg. N, for a titrimetric finish. Steam out the borosilicate-glass distillation apparatus illustrated in Fig. 48-6 (p. 2432) by boiling water in the flask until the distillate becomes free of  $\text{NH}_3$  as demonstrated with Nessler reagent.

Transfer 700 to 1000 ml. neutralized and dechlorinated sample into the 2-l. distilling flask along with several glass beads or boiling chips. Adjust the sample pH to 7.4, and collect 50 to 300 ml. distillate as described in "Ammonia Nitrogen." After the flask contents have cooled, introduce 50.0 ml. alkaline  $\text{KMnO}_4$  reagent, mix, and collect an additional 200 or 250 ml. distillate below the surface of 50 ml.

<sup>46</sup> Phelps, E. B., APHA Public Health Papers and Reports, 29, 354, 1903; J. Infectious Diseases, 1, 327, 1904.

$\text{H}_3\text{BO}_3$  if the albuminoid N exceeds 0.05 mg. Use a new receiver for this fraction. Cleanse the condenser by lowering the collected distillate free of the delivery tube during the last 1 or 2 min of distillation. Determine the  $\text{NH}_3$  content of the distillate as described in Ammonia Nitrogen. Correct the sample result by deducting the  $\text{NH}_3$  nitrogen content of 50.0 ml alkaline  $\text{KMnO}_4$  reagent carried through the entire procedure.

$$\text{Albuminoid N milligrams per liter} = \frac{A \times 1000}{\text{milliliters of sample}} \times \frac{B}{C}$$

where  $A$  = milligrams of  $\text{NH}_3$  nitrogen found colorimetrically or titrimetrically

$B$  = milliliters of total distillate collected including  $\text{H}_3\text{BO}_3$ , and

$C$  = milliliters of distillate taken for Nesslerization or titration

### KJELDAHL (ORGANIC) NITROGEN <sup>2 47</sup>

The  $\text{NH}_3$  nitrogen can be collected conveniently during the concentration phase of the procedure thereby enabling 2 determinations to be performed successfully on the same sample. The same considerations apply to prompt examination sample refrigeration or preservation and precautions against  $\text{NH}_3$  contamination is in the case of Ammonia Nitrogen above. The close similarities between the  $\text{NH}_3$  and Kjeldahl distillations dictate that the entire discussion on ammonia nitrogen should be studied before the organic N determination is undertaken. Electrical heat for the final Kjeldahl distillation minimizes bumping and presents fewer difficulties than are involved in the use of gas heat.

**Reagents** Deionized Distilled Water—This should be used for the preparation of all solutions and dilutions.

Appropriate Reagents Described Under Ammonia Nitrogen

**Digestion Solution** Dissolve 134 g  $\text{K}_2\text{SO}_4$  in 650 ml water and 200 ml concentrated  $\text{H}_2\text{SO}_4$ . Dissolve 2 g red  $\text{HgO}$  in 25 ml 6 N  $\text{H}_2\text{SO}_4$ . Combine the 2 solutions and dilute to 1 liter. Store at a temperature above 14°C to prevent crystallization.

**Sodium Hydroxide Sodium Thiosulfate Solution**—Dissolve 500 g  $\text{NaOH}$  and 20 g  $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$  in water and dilute to 1 liter.

**Phenolphthalein Indicator**

**Procedure**—Select a sample volume containing up to 1.0 mg Kjeldahl N if the distillate is to be Nesslerized or 0.5 to 5 mg N for a titrimetric finish.

Measure a 500 ml sample or a suitable aliquot into a steamed out 800-ml Kjeldahl flask together with 10 ml phosphate buffer solution and several glass beads or boiling chips. Evaporate 300 ml of the sample or distill and conserve this volume as described under Ammonia Nitrogen. Cautiously add 50 ml digestion solution to the cooled contents of the flask. Use an additional 50 ml digestion solution when a large quantity of non-nitrogenous organic matter is encountered. Mix thoroughly and resume evaporation in a fuming hood to the appearance of  $\text{SO}_3$  fumes. Digest for another 30 min after the acid concentrate turns colorless or a pale yellow color. Dilute the cooled digestate with 300 ml water and mix in 0.5 ml phenolphthalein indicator. Carefully introduce down the side of the tilted flask 50 ml (or more if the red phenolphthalein color fails to materialize as expected)  $\text{NaOH-N}_2\text{S}_2\text{O}_3$  solution so that the alkaline solution forms a distinct layer at the bottom. Immediately attach the flask to the steamed

<sup>4</sup> Morgan, G. B., Lackey, J. B. and Gilcreas, F. W. Anal. Chem. 23, 833 (1951)



out distillation apparatus, swirl the contents to achieve homogeneous dispersion and a red phenolphthalein color, and collect 200 ml. distillate below the surface of 50 ml.  $\text{H}_3\text{BO}_3$  solution. Cleanse the condenser by lowering the collected distillate free of the delivery tube during the last 1 or 2 min. of distillation. Determine the  $\text{NH}_3$  content of the distillate as described in "Nesslerization or Titration," under "Ammonia Nitrogen." Correct the sample result by deducting the  $\text{NH}_3$  nitrogen content of the reagent blank carried through the entire procedure used.

$$\text{Kjeldahl N, milligrams per liter} = \frac{A \times 1000}{\text{milliliters of sample}} \times \frac{B}{C}$$

where  $A$  = milligrams of  $\text{NH}_3$  nitrogen found colorimetrically or titrimetrically,

$B$  = milliliters of total distillate collected, including the  $\text{H}_3\text{BO}_3$ , and

$C$  = milliliters of distillate taken for Nesslerization or titration.

### CHEMICAL (DICHROMATE) OXYGEN DEMAND <sup>2, 11, 48</sup>

Aromatic hydrocarbons and pyridine resist oxidation by this method even in the presence of the  $\text{Ag}$  catalyst. The  $\text{Ag}_2\text{SO}_4$  catalyst reacts with  $\text{Cl}$ ,  $\text{Br}$ , and  $\text{I}$  to produce precipitates that are oxidized only partially by the procedure. In the absence of  $\text{Ag}_2\text{SO}_4$ , chloride is quantitatively oxidized to chlorine by the combination of acid,  $\text{K}_2\text{Cr}_2\text{O}_7$ , and carbonaceous organic matter. The chemical oxygen demand so consumed equals 0.23 mg. per liter for each 1.0 mg. per liter of  $\text{Cl}$ , a correction that can be calculated by performing a chloride determination on a separate sample aliquot.

**Reagents.** Standard Ferrous Ammonium Sulfate Titrant, 0.025  $N$ .—Dissolve 9.80 g.  $\text{Fe}(\text{NH}_4)_2(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$  in distilled water, add 20 ml. concentrated  $\text{H}_2\text{SO}_4$ , cool, and dilute to 1000 ml. Standardize by diluting 25.00 ml. standard 0.02500  $N$   $\text{K}_2\text{Cr}_2\text{O}_7$  to 275 ml., carefully adding 50 ml. concentrated  $\text{H}_2\text{SO}_4$ , cooling, and titrating with the  $\text{Fe}(\text{NH}_4)_2(\text{SO}_4)_2$  solution to the phenanthroline-ferrous sulfate indicator (8 to 10 drops) end point.

Standard Potassium Dichromate Solution, 0.02500  $N$ .—Dissolve 1.226 g.  $\text{K}_2\text{Cr}_2\text{O}_7$ , primary standard grade (dried at  $105^\circ\text{C}$ . for 2 hr.), in distilled water and dilute to 1000 ml.

Phenanthroline-Ferrous Sulfate Indicator.—Dissolve 1.485 g. 1,10-phenanthroline monohydrate and 0.695 g.  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$  in distilled water and dilute to 100 ml.

Sulfuric Acid, Concentrated.

Silver Sulfate.

**Procedure.**—Pipet into a 300- or 500-ml. flask a 50-ml., well-mixed sample, or dilute an aliquot to 50 ml. with distilled water. Add with a pipet 25 ml. standard 0.02500  $N$   $\text{K}_2\text{Cr}_2\text{O}_7$ , then stir in carefully and thoroughly 75 ml. concentrated  $\text{H}_2\text{SO}_4$ . (If the sample is known to contain straight-chain alcohols and organic acids, add 1 g.  $\text{Ag}_2\text{SO}_4$  at this point to catalyze the oxidation. Handle chloride interference by boiling the mixture of sample,  $\text{K}_2\text{Cr}_2\text{O}_7$ , and acid for 20 min., cooling the digestion mixture, adding 1 g.  $\text{Ag}_2\text{SO}_4$ , and resuming the reflux.) Add boiling chips or glass beads to prevent bumping, connect the ground-glass neck (24/40) of the flask with a Friedrichs condenser, reflux the mixture for 2 hr. or any shorter period known to yield maximum oxidation. After the flask contents have cooled, wash down the condenser with about 25 ml. distilled water, and

<sup>48</sup> Moore, W. A., Kroner, R. C., and Ruchhoft, C. C., *Anal. Chem.*, **21**, 953, 1949.

quantitatively transfer the mixture to a 500 ml flask with 4 to 5 distilled water washes. Dilute to about 350 ml with distilled water cool to room temperature add 8 to 10 drops phenanthroline ferrous sulfate indicator and titrate the residual  $\text{K}_2\text{Cr}_2\text{O}_7$  with standard 0.02N  $\text{Fe}(\text{NH}_4)_2(\text{SO}_4)_2$  until the color changes from blue to red. Carry a 50 ml distilled water blank through the entire procedure including the reflux operation.

$$\text{COD milligrams per liter} = \frac{(A - B) \times V \times 8000}{\text{milliliters of sample}} - C$$

where  $A$  = milliliters of  $\text{Fe}(\text{NH}_4)_2(\text{SO}_4)_2$  titration for blank

$B$  = milliliters of  $\text{Fe}(\text{NH}_4)_2(\text{SO}_4)_2$  titration for sample

$C$  = chloride correction = milligrams per liter of  $\text{Cl}^- \times 0.23$  and

$V$  = normality of  $\text{Fe}(\text{NH}_4)_2(\text{SO}_4)_2$  titrant

### OXYGEN CONSUMED FROM PERMANGANATE

Two versions of the oxygen consumed from permanganate method are in use for estimating the strength of organic pollution in streams. One modification hastens the oxidative reaction by elevating the sample temperature over a shorter time. The other determination is conducted near room temperature for an extended period. Since both procedures are empirical experimental conditions must be uniform for the results to have significance. Clean glassware is mandatory.

**Reagents** Standard Potassium Permanganate Solution 0.0125 N—Filter the supernatant from an aged solution of 0.1N  $\text{KMnO}_4$  through a fritted glass crucible and dilute 125 ml to 100 ml with distilled water. Standardize the solution daily as described under Calcium p 2410 above. The equivalence of 0.0125N  $\text{KMnO}_4$  is 0.100 mg oxygen consumed per 100 ml.

**Sulfuric Acid Solution** 1 + 3. Add 0.0125N  $\text{KMnO}_4$  solution until a very faint color persists after 4 hr.

**Sodium Sulfite Dechlorinating Solution** 0.025N—1.575 g per 100 ml.

**Reagents for Half Hour Method** Standard Ammonium Oxalate Solution 0.0125N. Dissolve 0.8882 g  $(\text{NH}_4)_2\text{C}_2\text{O}_4 \cdot \text{H}_2\text{O}$  dried at  $105^\circ\text{C}$  and dilute to 1000 ml with distilled water.

**Reagents for Four Hour Method** Standard Sodium Thiosulfate Titrant 0.0125N—In a 1 liter volumetric flask place 0.6 g  $\text{NaHCO}_3$  and dilute 125 ml 0.1N  $\text{Na}_2\text{S}_2\text{O}_3$  with distilled water. Prepare daily and standardize as described in Iodometric Method under Residual Chlorine p 2415 above.

**Starch Indicator**

**Potassium Iodide**

**Procedure**—When the residual chlorine exceeds 0.5 mg per liter dechlorinate the sample with a minute amount of 0.025N  $\text{Na}_2\text{SO}_3$  solution to the 0.05 mg per liter level. Do not dechlorinate completely.

**Half Hour Method**—Pipet 100 ml well mixed sample and 100 ml distilled water into separate 250 ml flasks and treat both the sample and blank alike throughout the procedure. Add 10 ml 1 + 3  $\text{H}_2\text{SO}_4$  and 10.00 ml standard 0.0125N  $\text{KMnO}_4$ . Immerse the flask in a boiling water bath for exactly 30 min making certain that the liquid level in the flask is completely submerged in the boiling water throughout the entire period. If the  $\text{KMnO}_4$  color in the sample grows faint or disappears take a smaller volume and dilute to 100 ml with distilled water before repeating the procedure. Introduce 10.00 ml standard 0.0125N

$(\text{NH}_4)_2\text{C}_2\text{O}_4$  solution, and, while still hot, titrate with standard 0.0125 *N*  $\text{KMnO}_4$  to a faint pink end point.

$$\text{Oxygen consumed from } \text{KMnO}_4, \text{ milligrams per liter} = \frac{(A - B) \times N \times 8000}{\text{milliliters of sample}}$$

where *A* = milliliters of titration for sample,

*B* = milliliters of titration for distilled water blank, and

*N* = normality of  $\text{KMnO}_4$  titrant.

**Four-Hour Method.**<sup>17</sup>—Measure 250 ml. well-mixed sample and 250 ml. distilled water into separate 400-ml., glass-stoppered bottles, and bring to 27°C. Treat both the sample and blank alike throughout the procedure. Add 10 ml. 1 + 3  $\text{H}_2\text{SO}_4$ . With a volumetric pipet introduce an appropriate volume of standard 0.0125 *N*  $\text{KMnO}_4$ . Select a  $\text{KMnO}_4$  volume in sufficient excess to require a back-titration of 5 to 15 ml. at the end of 4 hr.; and, in any case, use no less than 10.00 ml.  $\text{KMnO}_4$ . Gently rotate the bottle to mix the contents, and place in a water bath or incubator at 27°C. for exactly 4 hr. Several times during the incubation, mix, by gentle rotation, any sample that contains appreciable suspended matter. Cool to room temperature, add a few small crystals KI, mix, and titrate the contents of the bottles with standard 0.0125 *N*  $\text{Na}_2\text{S}_2\text{O}_3$  titrant. Add 1.0 ml. starch indicator when the color turns pale straw, and complete the titration to the first disappearance of the blue color.

Oxygen consumed from  $\text{KMnO}_4$ , milligrams per liter

$$= \frac{[(A - B) - (C \times D)] \times 8000}{\text{milliliters of sample}}$$

where *A* = milliliters of standard  $\text{KMnO}_4$  solution added,

*B* = normality of standard  $\text{KMnO}_4$  solution,

*C* = milliliters of standard  $\text{Na}_2\text{S}_2\text{O}_3$  titration, and

*D* = normality of standard  $\text{Na}_2\text{S}_2\text{O}_3$  titrant.

### DISSOLVED OXYGEN<sup>2, 11, 49, 50</sup>

The azide modification of determining dissolved oxygen is applicable to most waters that are not heavily polluted. Nitrite and ferrous ions must be less than 0.1 mg. per liter and 1 mg per liter, respectively. Appreciable quantities of such oxidants as hypochlorite and free chlorine, reductants such as sulfite, thiosulfate, and polythionate, and sugars and starches interfere. The addition of 1 ml. KF before acidification overcomes the effect of ferric concentrations below 200 mg. per liter, when the titration is completed without delay. An alternative to the use of KF in overcoming ferric interference resides in the substitution of  $\text{H}_3\text{PO}_4$  for  $\text{H}_2\text{SO}_4$  in the final acidification.

**Reagents.** Standard Sodium Thiosulfate Titrant, 0.025 *N*.—Dilute 250 ml. 0.1 *N*  $\text{Na}_2\text{S}_2\text{O}_3$  to 100 ml. with freshly boiled and cooled distilled water. Preserve with 5 ml.  $\text{CHCl}_3$ , or 0.4 g. NaOH, or 4 g.  $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$  and 10 mg.  $\text{HgI}_2$  for each liter of solution. Standardize daily as follows: dissolve 2 g. KI in 180 ml. distilled water contained in a flask; add 1 ml. concentrated  $\text{H}_2\text{SO}_4$  and 20.00 ml. standard 0.02500 *N*  $\text{KH}(\text{IO}_3)_2$ , and titrate with the  $\text{Na}_2\text{S}_2\text{O}_3$  titrant to the first dis-

<sup>49</sup> Alsterberg, G., *Biochem. Z.*, 159, 36, 1925.

<sup>50</sup> Placak, O. R., and Ruchhoft, C. C., *Ind. Eng. Chem., Anal. Ed.*, 13, 12, 1941.

appearance of the blue starch indicator color. The equivalence of 0.02500  $\text{N}$   $\text{Na}_2\text{S}_2\text{O}_3$  is 0.200 mg dissolved oxygen per 100 ml.

**Standard Potassium Biiodate Solution, 0.02500 N**—Dissolve 0.8124 g  $\text{KH}(\text{IO}_3)_2$  primary standard grade (dried at  $105^\circ\text{C}$ ) and dilute to 1000 ml with distilled water.

**Manganous Sulfate Solution**—Dissolve 480 g  $\text{MnSO}_4 \cdot 4\text{H}_2\text{O}$  or 400 g  $\text{MnSO}_4 \cdot 2\text{H}_2\text{O}$  or 364 g  $\text{MnSO}_4 \cdot \text{H}_2\text{O}$  in distilled water, filter and dilute to 1 liter.

**Alkaline Iodide Azide Solution**—Dissolve 500 g  $\text{NaOH}$  (or 700 g  $\text{KOH}$ ) and 135 g  $\text{NaI}$  (or 150 g  $\text{KI}$ ) in distilled water and dilute to 1 liter. Dissolve 10 g  $\text{NaN}_3$  in 40 ml distilled water and add to the alkaline iodide solution.

**Potassium Fluoride Solution**—40 g  $\text{KF} \cdot 2\text{H}_2\text{O}$  per 100 ml.

**Starch Indicator**

**Sulfuric Acid Concentrated**

**Procedure**—Collect the dissolved oxygen sample and add 1 ml  $\text{KF}$  solution, 2 ml  $\text{MnSO}_4$  solution, 2 ml alkaline iodide azide reagent and 2 ml concentrated  $\text{H}_2\text{SO}_4$  as described in the second method for preservation of dissolved oxygen under "Collection of Sample" p. 2395 above. From the sample bottle remove 200 ml of the treated sample, place in a 500 ml flask and titrate the liberated iodine with standard 0.025  $\text{N}$   $\text{Na}_2\text{S}_2\text{O}_3$ . Add 1 to 2 ml starch indicator when the color turns pale straw and complete the titration to the first disappearance of the blue color. Ignore the reappearance of a blue color caused by nitrite and ferrous ions.

Correct the 200 ml sample aliquot for the reagents added to a 300 ml bottle as follows:

$$\text{Corrected sample aliquot} = 200 \times \frac{300}{300 - y}$$

where  $y$  represents the total volume of reagents added to the sample bottle (if 1 ml  $\text{KF}$ , 2 ml  $\text{MnSO}_4$  and 2 ml alkaline iodide azide reagent are all used,  $y = 1 + 2 + 2 = 5$ ).

Calculate the dissolved oxygen by substituting in the following equation:

$$\text{DO (milligrams per liter)} = \frac{A \times N \times 8000}{B}$$

where  $A$  = milliliters of titration for sample aliquot,

$B$  = milliliters of corrected sample aliquot, and

$N$  = normality of  $\text{Na}_2\text{S}_2\text{O}_3$ .

To express the results in milliliters of oxygen gas per liter at  $0^\circ\text{C}$  and 760 mm pressure, multiply milligrams per liter of dissolved oxygen by 0.698.

## BIOCHEMICAL OXYGEN DEMAND (BOD)\*

The biochemical oxygen demand (BOD) assesses the degree of stream pollution by measuring the oxygen consumed through bacterial and chemical action in a closed sample held at  $20^\circ \pm 1^\circ\text{C}$  for 5 days. For this reason the dilution water should be free of any agents likely to inhibit bacterial activity and should be saturated with oxygen.

This determination is affected by the quality of the dilution water, the effectiveness of the seed, and the technique of the analyst. Storage vessels for dilution water and incubation bottles should be regularly cleaned with a good detergent, thoroughly rinsed and drained to minimize contamination. A good quality dilution water should be saturated with air at  $20^\circ\text{C}$  to a dissolved oxygen level of

approximately 9 mg. per liter. Precautions should be observed at all times to avoid oxygen supersaturation in both the dilution water and the sample. Any preliminary heating of the sample to 20°C. should be carried out in a manner to keep oxygen supersaturation at a minimum; otherwise, the subsequent loss during incubation will lead to fictitiously high results. The importance of the proper seed cannot be overemphasized with respect to industrial discharges. Some sewage seeds are relatively ineffective for such situations and yield low B.O.D. values. Past experience is the best guide for determining the amount and type of seed suitable for a particular sample or group of samples.

Clean and fairly clean river waters seldom exhibit a B.O.D. in excess of 3 mg. per liter; therefore, samples from such sources can be run without dilution. The B.O.D. of river waters of doubtful purity, on the other hand, may exceed 5 mg. per liter, with polluted streams approaching 10 mg. per liter or more. The latter samples obviously must be diluted.

**Reagents.**—Distilled water of the highest quality should be used for the preparation of all solutions and dilution water. Stills constructed of block tin or glass will yield the required distillate, which must be free from Cu, chlorine, chloramines, caustic alkalinity, organic material, or acids.

**Stock Solutions for the Preparation of Dilution Water. Phosphate Buffer Solution, pH 7.2.**—Dissolve 8.5 g.  $\text{KH}_2\text{PO}_4$ , 21.75 g.  $\text{K}_2\text{HPO}_4$ , 33.4 g.  $\text{Na}_2\text{HPO}_4 \cdot 7\text{H}_2\text{O}$  (or 17.7 g.  $\text{Na}_2\text{HPO}_4$ ), and 1.7 g.  $\text{NH}_4\text{Cl}$  in 500 ml. distilled water and dilute to 1 liter. Add this buffer just before the dilution water is to be used.

**Magnesium Sulfate Solution.**—22.5 g.  $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$  per liter.

**Calcium Chloride Solution.**—27.5 g.  $\text{CaCl}_2$  per liter.

**Ferric Chloride Solution.**—0.25 g.  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  per liter.

**Preparation of Dilution Water.**—Aerate the distilled water at 20°C. by: allowing a cotton-plugged bottle to stand 2 to 3 days until the distilled water becomes saturated with atmospheric oxygen; shaking a partially filled bottle of distilled water to absorb atmospheric oxygen; or bubbling clean compressed air through the distilled water. Place the required volume of distilled water in a suitable bottle and add to each liter 1.0 ml. of each of the stock solutions. Discard unused dilution water after 1 week's storage to prevent errors arising from possible nitrification. If necessary, seed each liter of the dilution water with sewage organisms in one of the following ways: add 1 to 10 ml. settled domestic sewage that is 24 to 36 hr. old; add 1 drop lactose broth from a bacteriological tube, which tests positively for coliform organisms; add 10 to 50 ml. river water. Select that amount of seed which produces an oxygen depletion in the blank of no less than 0.6 mg. per liter after 5 days' incubation. Use the seeded dilution water only on the day it is made.

**Sodium Sulfite Dechlorinating Solution, 0.025 N.**—1.575 g. per 1000 ml.

**Bromthymol Blue Indicator Solution.**—0.1 g. per 100 ml.

**All Reagents Required for the Dissolved Oxygen Determination.**

**Sulfuric Acid, 1 N.**

**Sodium Hydroxide, 1 N.**

**Procedure. Pretreatment.**—(a) Neutralize a sample containing caustic alkalinity or acidity to pH 7.0 by adding 1 N  $\text{H}_2\text{SO}_4$  or 1 N  $\text{NaOH}$ . Use a pH meter or bromthymol blue as an external indicator. (b) Allow residual chlorine concentrations of 0.1 mg. per liter or less to dissipate by standing 1 to 2 hr. Treat higher chlorine residuals by determining the residual chlorine concentration, and then adding the exact amount of 0.025 N  $\text{Na}_2\text{SO}_3$  solution to reduce the chlorine. (c) Place the sample supersaturated with dissolved oxygen in a partly filled bottle, carefully bring the temperature to 20°C. (warming if necessary), and shake vigor-

ously or aerate with compressed air (d) If the dissolved oxygen content of the sample exceeds 9.2 mg per liter or falls below 6.9 mg per liter shake the sample vigorously to saturate with atmospheric oxygen using a partially filled bottle for the shaking operation then carefully siphon the oxygen saturated sample into duplicate 300 ml BOD bottles

**Treatment of Undiluted Sample**—When the BOD value of the water sample is less than 5.0 mg per liter fill two 300 ml BOD bottles to overflowing tightly stopper 15 min later without entraining air bubbles place 1 bottle in a  $20^{\circ} \pm 1^{\circ}\text{C}$  air incubator for 5 days and determine the immediate dissolved oxygen of the sample in the second bottle Protect the bottle contents against the entry of air by adding water to the flared mouth of the BOD bottle or by inverting the BOD bottles in a tray of water Use a constant temperature water bath set at  $20 \pm 1^{\circ}\text{C}$  in place of an unavailable incubator Cover the bath to exclude any penetration of light into the bottles

**Preparation of Sample Dilutions**—When the BOD value exceeds 5.0 mg per liter prepare such sample dilutions as 1 + 1 1 + 2 1 + 3 or 1 + 4 so that no more than one half to two thirds of the oxygen will be consumed in the dilution during incubation Use 1 of the following 2 approaches (a) Carefully siphon standard dilution water seeded if necessary into a 1 or 2 l graduated cylinder Fill the cylinder half full without undue aeration of the contents Add the proper volume of carefully mixed sample to secure the desired dilution and dilute to the appropriate mark with dilution water Mix gently but thoroughly with a plunger type rod guarding against air entrainment Siphon the mixed dilution into two 300 ml BOD bottles and fill to the top so that the glass stopper can be tightly inserted into the bottle 15 min later without entraining air bubbles Place 1 bottle in a  $20 \pm 1^{\circ}\text{C}$  air incubator for 5 days and save the other bottle for the immediate determination of the dissolved oxygen content of the diluted sample Water seal and incubate as prescribed under Treatment of Undiluted Sample immediately above (b) With a large tip volumetric pipet add a definite volume of sample to a 300 ml BOD bottle of exactly known capacity fill the bottle with dilution water to the top and tightly stopper 15 min later without entraining air bubbles Water seal and incubate as directed under Treatment of Undiluted Sample

**Determination of Dissolved Oxygen**—Complete the determination as directed under Dissolved Oxygen p 2457 above

**Seed Correction**—Determine the oxygen absorption of the seed by preparing a series of seed dilutions Reject those dilutions that fail to give a 40 to 70% oxygen depletion for 5 days Use 1 of the depletions in the accepted range to calculate the correction due to the small amount of seed in the dilution water

**Technique Check**—Check the quality of the unseeded dilution water by filling 2 bottles in the accepted manner incubating 1 bottle along with the diluted samples and determining the dissolved oxygen before and after incubation Even though the oxygen depletion should be less than 0.2 ml and preferably less than 0.1 ml do not apply the results as a blank correction

**Calculations For an Undiluted Sample**—

BOD, milligrams per liter =  $DO_{15 \text{ min after preparation}} - DO_{\text{after incubation}}$

**For a Diluted and Unseeded Sample**—

$$\text{BOD milligrams per liter} = \frac{D_1 - D_2}{P}$$

*For a Diluted and Seeded Sample.—*

$$\text{B.O.D., milligrams per liter} = \frac{(D_1 - D_2) - (B_1 - B_2)f}{P}$$

where  $DO$  = dissolved oxygen content in milligrams per liter,

$D_1$  =  $DO$  of diluted sample 15 min. after preparation,

$D_2$  =  $DO$  of diluted sample after incubation,

$P$  = decimal fraction of sample used

=  $\frac{\text{milliliters of dilution water} + \text{milliliters of sample}}{\text{milliliters of sample}}$

$B_1$  =  $DO$  of dilution of seed control before incubation,

$B_2$  =  $DO$  of dilution of seed control after incubation, and

$f$  =  $\frac{\text{percentage of seed in diluted sample } D_1}{\text{percentage of seed in control } B_1}$ .

Accept as most reliable those sample dilutions showing a residual dissolved oxygen of at least 1 mg. per liter, a minimum oxygen depletion of 2 mg. per liter, or those dilutions where no more than one-half to two-thirds of the oxygen is consumed.

### RESIDUAL OZONE <sup>2</sup>

The iodometric titration of residual  $O_3$  is the method of choice because of its reliability, acceptable precision, and susceptibility to fewest interferences. The orthotolidine-arsenite (OTA) method is satisfactory for routine estimations when  $O_3$  is applied to a water supply for disinfection or taste and odor control. Since other strong oxidants are normally absent in waters of potable quality, the resulting yellow color is proportional to the  $O_3$  concentration.

The instability of residual  $O_3$  and the impossibility of preservation dictate the prompt performance of the determination. Sample aeration should be kept at a minimum during collection to avoid  $O_3$  loss.

### IODOMETRIC METHOD

**Reagents.** Standard Sodium Thiosulfate Titrant, 0.005  $N$ .—Dilute 50 ml. 0.1  $N$   $Na_2S_2O_3$  to 1000 ml. with distilled water. Standardize daily against standard 0.005000  $N$   $KH(IO_3)_2$ , using the same volumes of KI solution, concentrated  $H_2SO_4$ , and starch indicator as in the actual sample titration. The equivalence of 0.0050  $N$   $Na_2S_2O_3$  is 0.120 mg.  $O_3$  per 1.00 ml.

**Standard Potassium Bi-iodate Solution, 0.005000  $N$ .**—Dissolve 0.1625 g.  $KH(IO_3)_2$ , primary standard grade (dried at 105°C.), and dilute to 1000 ml. with distilled water.

**Potassium Iodide Absorbant Solution.**—Dissolve 20 g. KI in 1 liter freshly boiled and cooled distilled water. Store in an amber bottle.

**Sulfuric Acid, Concentrated.**

**Starch Indicator.**

**Procedure.**—Taking precautions to minimize  $O_3$  loss through aeration, collect an 800-ml. sample in a 1-liter, standard gas washing bottle with a medium-permeability, porous-plate diffuser at the bottom. With a stream of pure air or nitrogen sweep all the  $O_3$  from the sample into the 500-ml. absorber containing 400 ml. KI absorbant solution at a rate of 200 to 1000 ml. per minute for 5 min. Transfer and rinse the KI absorbant into a 1000-ml., white porcelain casserole, flask, or beaker, and add 1 ml. concentrated  $H_2SO_4$  or sufficient acid to reduce the pH below 2.0.

Immediately titrate with standard 0.005  $N$   $Na_2S_2O_3$ . Add 4 ml. starch indicator when the color turns pale straw and complete the titration to the first disappearance of the blue color. Determine the blank titration by taking 400 ml.  $KI$  solution 1 ml. concentrated  $H_2SO_4$  and 4 ml. starch indicator through the entire procedure

$$O_3, \text{ milligrams per liter} = \frac{(A - B) \times N \times 24000}{\text{milliliters of sample}}$$

where  $A$  = milliliters of titration for sample,  
 $B$  = milliliters of titration for blank, and  
 $N$  = normality of  $Na_2S_2O_3$

#### ORTHOTOLIDINE ARSENITE (OTA) METHOD

The *o*-tolidine and  $NaAsO_2$  reagents, chromate-dichromate color standards and apparatus employed in the OTA method for  $O_3$  are the same as those used in the OTA method for residual chlorine. On the average the yellow color developed by  $O_3$  approximates that of a comparable quantity of chlorine.

**Procedure.**—Use 0.5 ml. *o*-tolidine reagent and 0.5 ml.  $NaAsO_2$  solution for each 9.5 ml. sample taken. Place the proper volume of *o*-tolidine reagent in the tube or bottle and add a measured volume of water sample. Mix rapidly and thoroughly and within 5 sec. add the proper volume of  $NaAsO_2$  solution. Mix again and promptly compare the color against permanent color standards. Record as reading  $A$ . Into a second tube or bottle place a similar volume of  $NaAsO_2$  solution followed by the same volume of water sample used for the first tube or bottle. Mix rapidly and thoroughly, and add the original volume of *o*-tolidine reagent. Mix again and promptly compare the color against permanent color standards. Record as reading  $B$ .

$$O_3, \text{ milligrams per liter} = \text{reading } A - \text{reading } B$$

#### pH VALUE<sup>2, 11</sup>

The best results are achieved with an assembly whereby the sample water flows at its natural temperature directly past the electrode system. In the absence of this ideal arrangement the pH should be determined at the time of sample collection, or as soon thereafter as possible. If a sample must be transported to the laboratory, the determination should be performed immediately after the sample bottle is opened. These precautions are necessary because the pH obtained in the laboratory may differ from the actual and true pH, by virtue of reactions that may occur within the sample upon standing. Among the sample reactions that can influence a delayed result are oxidation, hydrolysis, interactions with the sediment, loss of dissolved gases, absorption of laboratory fumes, and deposition of  $CaCO_3$  or other salts.

**Reagents. Buffer Solutions.**—All the salts used in the preparation of the following buffer solutions should be dried for 1 hr. at  $110^\circ$  to  $130^\circ C$ , and cooled to room temperature in a desiccator. The exceptions are  $Na_2B_4O_7 \cdot 10H_2O$  and  $KH_2C_4O_6 \cdot 2H_2O$ , the latter should not be heated above  $60^\circ C$ . The pH of the standard buffer solutions is given in Table 48.8.

**Boiled Distilled Water.**—This should be used for the preparation of all buffer solutions.

**Potassium Tetroxalate Solution, 0.05  $M$ .**—12.70 g.  $KH_3C_4O_8 \cdot 2H_2O$  per 1000 ml.



TABLE 48-8. pH OF STANDARD BUFFER SOLUTIONS

Temp., °C.	0.05 <i>M</i> Potas- sium Tetrox- alate Solution	Satd. Tar- trate Solu- tion	0.05 <i>M</i> Phthal- ate Solu- tion	0.025 <i>M</i> Phos- phate Solu- tion	0.01 <i>M</i> Borax Solu- tion	0.0203 <i>M</i> Calcium Hydroxide Solution
0	1.67	—	4.01	6.98	9.46	13.43
10	1.67	—	4.00	6.92	9.33	13.00
20	1.68	—	4.00	6.88	9.22	12.63
25	1.68	3.56	4.01	6.86	9.18	12.45
30	1.69	3.55	4.01	6.85	9.14	12.30
35	1.69	3.54	4.02	6.84	9.10	12.14
40	1.70	3.54	4.03	6.84	9.07	11.99
50	1.71	3.55	4.06	6.83	9.01	11.70
60	1.73	3.57	4.10	6.84	8.96	11.45

**Saturated Potassium Acid Tartrate Solution.**—Prepare by shaking vigorously excess  $\text{KHC}_4\text{H}_4\text{O}_6$  with 100 to 300 ml. water in a glass-stoppered bottle. Filter if necessary, and preserve with 0.1 g. thymol.

**Potassium Acid Phthalate Solution, 0.05 *M*.**—10.21 g.  $\text{KHC}_8\text{H}_4\text{O}_4$  per 1000 ml.

**Phosphate Solution, 0.025 *M*.**—Dissolve 3.44 g.  $\text{KH}_2\text{PO}_4$  and 3.55 g.  $\text{Na}_2\text{HPO}_4$  and dilute to 1000 ml.

**Borax Solution, 0.01 *M*.**—3.81 g.  $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$  per 1000 ml.

**Saturated Calcium Hydroxide Solution.**—Prepare pure  $\text{Ca}(\text{OH})_2$  from well-washed  $\text{CaCO}_3$  of low-alkali grade. Heat the carbonate slowly to  $1000^\circ\text{C}$ ., and ignite for at least 45 min. at that temperature. After cooling, add the  $\text{CaO}$  slowly to distilled water with stirring, heat the suspension to boiling, cool, and filter on a sintered-glass funnel of medium porosity. Dry the solid in an oven, and crush to a uniform finely divided state. Shake a considerable excess of the hydroxide vigorously with distilled water at room temperature in a stoppered bottle. Allow the gross excess of solid to settle, record the temperature to the nearest degree C., and filter the supernatant with suction through a sintered-glass funnel of medium porosity. Correct column 2 of the following table for the temperature of saturation according to the data below.

Sat. Temp., °C.	Solu- bility, <i>M</i>	pH at °C.			Correction
		20	25	30	
20	0.0211	12.64	12.47	12.31	+0.015
25	0.0203	12.63	12.45	12.30	0
30	0.0195	12.61	12.44	12.28	−0.016

Replace when turbidity appears as a result of the contamination of the filtered sample with atmospheric  $\text{CO}_2$ .

A buffer solution should be discarded when mold growth or contamination occurs.

**Procedure**—The differences among the makes and models of pH meters available commercially render impossible the formulation of a set of detailed instructions applicable to every satisfactory instrument. For this reason the manufacturer's recommendations for the care and operation of both the electrodes and the meter should be followed. The glass electrode and the calomel electrode should be thoroughly wetted and prepared for use as specified for the particular instrument at hand. The instrument should then be standardized under conditions of temperature and concentration as close as possible to those of the sample using a buffer solution of pH approaching that of the sample. The linearity of electrode response should next be confirmed against at least one additional buffer of a different pH. The electrodes should be washed free of buffer solution with distilled water and finally with the sample. The electrodes should be left in the sample for several minutes to obtain a stable reading. A final check can be made by immersing the electrodes in a fresh portion of the sample. The sample should be subjected to a minimum of aeration and agitation during the entire procedure. Since calomel electrodes deteriorate above 90°C, a silver-silver chloride reference electrode should be substituted for measurements at elevated temperatures. The error caused by high Na ion concentrations at pH measurements above 10 may be reduced by using low sodium error electrodes. Approximate correction for the Na error with ordinary glass electrodes may be made by consulting a chart furnished by the manufacturer.

Temperature exerts 2 significant effects on pH measurements: the potential developed by the electrode varies with temperature and ionization in the sample varies with temperature. The first effect can be compensated for by an adjustment provided on the better commercial instruments. The second effect is inherent in the sample and is taken into consideration by recording both the temperature and the pH of each sample.

## PHENOLS<sup>2, 51</sup>

The 4-aminoantipyrine reagent reacts with a group of hydroxy derivatives of benzene encompassing phenol, ortho and meta-substituted phenols and those para-substituted phenols in which the substituent consists of a carboxyl, halogen, methoxyl, hydroxy or sulfonic acid group. Insensitive to the reagent are *p*-cresol and similar para-substituted derivatives. The phenol result obtained by the 4-aminoantipyrine method represents the minimum concentration of the phenols in the sample for the reason that the molecular weights of the reactive phenolic compounds may be higher than phenol and the spectral absorption characteristics of the resulting colors may differ slightly from that of phenol.

The following interferences should be removed in advance of distillation. Oxidants should be reduced immediately with an excess of  $\text{FeSO}_4$  or  $\text{NaAsO}_2$  until a negative test is obtained with starch-iodide paper. Sulfur compounds should be eliminated at once by adding several drops of methyl orange indicator and enough  $\text{H}_3\text{PO}_4$  solution to lower the pH of the sample below 4.0, then aerating briefly by stirring before the  $\text{CuSO}_4$  is applied. Phenols in oils and tars should be reclaimed in advance of  $\text{CuSO}_4$  addition by adjusting the sample pH to 12 to 12.5 with con-

<sup>51</sup> Ettinger, M. B., Rudolph, C. C. and Liska, R. J. *Anal. Chem.* 23, 1783 (1951).

concentrated caustic, extracting the oil and tar from the aqueous phase by means of  $\text{CCl}_4$ , and finally driving off the residual  $\text{CCl}_4$  in the sample by warming on a water bath.

Oxidants and reductants, metallic ions that react with  $\text{K}_3\text{Fe}(\text{CN})_6$ , and aromatic amines that react with 4-aminoantipyrine interfere with the colorimetric determination, and, therefore, must be absent. On this account, samples of unfamiliar waters should be distilled in order to secure a reliable result. Time, temperature, and pH should be carefully controlled in the sample and standards to minimize the effect of these variables on color development.

When the determination must be delayed, the sample should promptly be acidified with  $\text{H}_3\text{PO}_4$  solution to a pH below 4.0, using methyl orange indicator, and preserved by the addition of 1 g.  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  to each liter of sample. The sample should be refrigerated until the analysis is begun as soon as possible, preferably within 24 hr.

*Reagents for Distillation.* Copper Sulfate Solution.—100 g.  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  per liter.

Phosphoric Acid Solution.—Dilute 10 ml. 85%  $\text{H}_3\text{PO}_4$  to 100 ml. with distilled water.

Sodium Hydroxide, 1 *N*.

Chloroform.

Sodium Chloride.

Methyl Orange Indicator.

*Reagents for Color Development.* Standard Phenol Solution.—(a) Dissolve 1.00 g. phenol in distilled water, and dilute to 1000 ml. Standardize by mixing in a glass-stoppered flask 50.00 ml. stock phenol solution, 100 ml. distilled water, 40.00 ml. standard 0.1000 *N* bromate-bromide solution, and 5 ml. concentrated HCl. After the reaction has proceeded for 10 minutes in the stoppered flask, add 1 g. KI, and titrate with standard 0.025 *N*  $\text{Na}_2\text{S}_2\text{O}_3$  (prepared and standardized as described in "Standard Sodium Thiosulfate Titrant, 0.025 *N*," p. 2457, above, under, "Dissolved Oxygen") to the first disappearance of the blue starch indicator color. Treat a blank containing 10.00 ml. standard 0.1000 *N* bromate-bromide solution, 150 ml. distilled water, and 5 ml. concentrated HCl in exactly the same manner. Calculate the phenol content of the stock solution by the following equation:

$$\text{Phenol, milligrams per liter} = (4B - A) \times 7.842$$

where *A* = milliliters of titration for phenol, and

*B* = milliliters of titration for blank.

(b) Dilute 10.00 ml. stock solution with distilled water to 1000 ml. for an intermediate dilution. (c) Then dilute 50.00 ml. intermediate dilution to 500 ml. to give a standard solution containing 0.001 mg. phenol per 1.00 ml. Prepare the intermediate and standard solutions daily.

4-Aminoantipyrine Solution, 2.0 g. per 100 ml.—Prepare daily.

Ammonium Chloride Solution, 50 g. per liter.

Potassium Ferricyanide Solution, 8 g. per 100 ml.—Filter if necessary and prepare weekly.

Ammonium Hydroxide, Concentrated.

Chloroform.

Sodium Sulfate.

$$\text{Phenols, milligrams per liter} = \frac{A \times 1000}{\text{milliliters of sample}} \times \frac{B}{C}$$

where  $A$  = milligrams of phenol found photometrically or visually. The ratio  $B/C$  applies only when a sample is distilled, the volume then made up to  $B$ , and an aliquot,  $C$ , taken from it for color development.

### PHOSPHATE <sup>2, 11</sup>

The  $\text{SnCl}_2$  method is suitable for determinations in the  $\text{PO}_4$  range of 0.05 to 3 mg. per liter, while the aminonaphtholsulfonic acid method finds greatest use in the range of 0.1 to 30 mg. per liter.

Color, turbidity, As, and Ge must be absent in both colorimetric methods. Sulfide can be oxidized with a minimal amount of free halogens such as saturated bromine or chlorine water to an innocuous form. The residual bromine and chlorine should then be completely removed by boiling or ultraviolet irradiation. The low results experienced with brines may be overcome by resorting to successive dilutions until an essentially consistent  $\text{PO}_4$  value is obtained. Slightly high  $\text{PO}_4$  values are possible in the presence of inordinate polyphosphate concentrations. Tolerable concentrations for soluble silicate are 100 mg. per liter in the aminonaphtholsulfonic acid method and 25 mg. per liter in the  $\text{SnCl}_2$  method. Since  $\text{SiO}_2$  yields an additive color, a correction can be applied when necessary. The upper limit for the dissolved Fe concentration is 0.1 mg. in the portion taken for analysis in the aminonaphtholsulfonic acid method, and 0.04 mg. in the  $\text{SnCl}_2$  method. Nitrite interference (bleaching of the blue color) in the  $\text{SnCl}_2$  method can be combatted by adding 0.1 g. sulfamic acid to the sample before introduction of the molybdate reagent. Chromate and strong oxidants, such as  $\text{H}_2\text{O}_2$ , bleach the blue color in the  $\text{SnCl}_2$  method. Lignin, tannin, and hexavalent Cr may interfere in both methods at  $\text{PO}_4$  levels below 1 mg. per liter. Barium, Pb, Hg, and Ag interfere by forming a precipitate in the  $\text{SnCl}_2$  method.

A field analysis is desirable when  $\text{PO}_4$  precipitates in the sample on standing. Microbiological activity can be repressed somewhat by the addition of 5 ml.  $\text{CHCl}_3$  to each liter of sample and refrigeration.

**Reagents.** Standard Phosphate Solution.—(a) Dissolve 0.7165 g.  $\text{KH}_2\text{PO}_4$ , dried at  $105^\circ\text{C}$ ., in distilled water, and dilute to 1000 ml. Add 5 ml.  $\text{CHCl}_3$ , and store in the dark to retard biological growth. (b) Dilute 100.0 ml. stock solution to 1000 ml. to form a standard solution containing 0.050 mg.  $\text{PO}_4$  per 1.00 ml. Prepare frequently and at least monthly.

**Strong Acid Solution.**—Cautiously add 300 ml. concentrated  $\text{H}_2\text{SO}_4$  to 600 ml. distilled water. After the mixed solution has cooled to room temperature, add 4.0 ml. concentrated  $\text{HNO}_3$ , and dilute to 1 liter.

**Activated Carbon.**—Nordite A, a product of American Nordite Co., Jacksonville, Fla., has proved satisfactory.

**Sodium Hydroxide,** 6 N.

**Phenolphthalein Indicator.**

**Reagents for Stannous Chloride Method.** Ammonium Molybdate Reagent.—(a) Dissolve 25 g.  $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$  in 175 ml. distilled water. (b) Cautiously add 280 ml. concentrated  $\text{H}_2\text{SO}_4$  to 400 ml. distilled water. (c) After solution (b) has cooled to room temperature, add solution (a) to solution (b), never the reverse, and dilute to 1 liter.

**Stannous Chloride Reagent**—Dissolve 25 g fresh  $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$  in 100 ml of glycerol. Heat in a water bath and stir with a glass rod to hasten dissolution. This reagent is stable and requires neither preservative nor special storage.

**Reagents for Aminonaphtholsulfonic Acid Method** **Ammonium Molybdate Reagent**—(a) Dissolve 31.4 g  $(\text{NH}_4)_6\text{MoO}_4 \cdot 4\text{H}_2\text{O}$  in 200 ml distilled water. (b) Cautiously add 252 ml concentrated  $\text{H}_2\text{SO}_4$  to 400 ml distilled water. After the mixed solution has cooled to room temperature add 3.4 ml concentrated  $\text{HNO}_3$ . (c) Prepare the reagent by adding solution (a) to solution (b) never the reverse and diluting to 1 liter.

**Aminonaphtholsulfonic Acid Reagent**—Weigh out separately 0.75 g 1-amino-2-naphthol-4-sulfonic acid (use a powder no darker than a pale pink in color) 42 g  $\text{Na}_2\text{SO}_3$  and 70 g  $\text{Na}_2\text{S O}_3$ . Pulverize the aminonaphtholsulfonic acid with a small proportion of the  $\text{Na}_2\text{S O}_3$  in a clean dry mortar. Dissolve the remaining  $\text{Na}_2\text{SO}_3$  and  $\text{Na}_2\text{S O}_3$  in 900 ml distilled water, add the finely ground aminonaphtholsulfonic acid  $\text{Na}_2\text{S O}_3$  mixture and stir to dissolve. Dilute to 1 liter. Store in a brown glass stoppered bottle at a temperature below  $30^\circ\text{C}$ .

**Procedure** **Preparation of Glassware**—Remove phosphate contamination from all glassware by filling each cleaned container with distilled water. Add with mixing 2 ml ammonium molybdate reagent, 1 ml strong acid solution and 1 ml  $\text{SnCl}_2$  reagent or aminonaphtholsulfonic acid reagent. Allow the reaction mixture to touch all of the interior of the container for at least 15 min. Drain, rinse thoroughly with distilled water and reserve this glassware solely for the  $\text{PO}_4$  determination. Repeat this treatment whenever detergents or phosphate compounds are used for cleaning.

**Preliminary Treatment of Sample**—If necessary, clarify the sample by centrifuging or filtration. Select a filter paper demonstrably free of  $\text{PO}_4$  or alternatively use any of the other appropriate filters mentioned under Residue (Solids) p 94 below. Reject the first 25 ml filtrate as insurance against contamination and possible adsorptive losses.

If necessary, remove interfering color by treating a 200 ml sample with two 0.25 g portions activated carbon demonstrably without effect on the  $\text{PO}_4$  concentration. Shake vigorously for 1 min after each carbon addition and pass through a dry medium textured filter paper. Determine the  $\text{PO}_4$  or polyphosphate in the filtrate by either the  $\text{SnCl}_2$  method or the aminonaphtholsulfonic acid method.

**Color Development by Stannous Chloride Method**—Pipet into a beaker 100 ml clear and colorless sample containing the following  $\text{PO}_4$  concentrations: 0.1 to 0.6 mg if a 0.5 cm cell will be used for the photometric reading; 0.03 to 0.3 mg for a 2-cm cell and 0.009 to 0.05 mg for a 10 cm cell. If necessary, dilute an appropriate aliquot to 100 ml with distilled water. Add 1 to 2 drops (0.05 to 0.10 ml) phenolphthalein indicator and sufficient strong acid solution dropwise to discharge any resultant pink color. Take a smaller sample volume if more than 5 drops strong acid solution are required, neutralize and dilute to 100 ml with distilled water. Prepare a blank and a series of  $\text{PO}_4$  standards in 100 ml volume with distilled water. Treat the blank and standards exactly as the sample throughout the procedure. Adjust the temperature of the blank standards sample and reagents so that all are in the  $20^\circ$  to  $30^\circ\text{C}$  range and the difference is no greater than  $\pm 2^\circ\text{C}$  among the entire set. Mixing after each addition, introduce 40 ml ammonium molybdate reagent and 0.5 ml (10 drops)  $\text{SnCl}_2$  reagent. Within 10 to 12 min determine the absorbance at 630  $\text{m}\mu$  preferably or at 650  $\text{m}\mu$  in a spectro-

photometer, or at 600 to 700  $m\mu$  in a filter photometer. The upper portions of the calibration curve may deviate from linearity.

When reliance must be placed on visual color matching, prepare  $PO_4$  standards of 0, 0.0025, 0.005, 0.015, and 0.025 mg. in 50-ml. Nessler tubes, and dilute to the mark with distilled water. Transfer only 50 ml. of the developed sample to a comparable Nessler tube, and match the colors of the sample and standards.

**Color Development by Aminonaphtholsulfonic Acid Method.**—Pipet 50 ml. clear and colorless sample into a 100-ml. volumetric flask if the pH of the sample is less than 4, and dilute to the mark with distilled water. Adjust the pH of a sample above 10 by discharging the pink phenolphthalein color of a 50.0-ml. portion with strong acid solution before diluting to 100 ml. (Use the figure 25 ml. for the diluted sample volume in the calculation, even though 50 ml. of the diluted sample is taken in the succeeding steps.) Pipet into a beaker or flask 50 ml. clear, colorless, and pH-adjusted sample containing the following  $PO_4$  concentrations: 0.25 to 1.5 mg. if a 0.5-cm. cell will be used for the photometric reading, 0.025 to 0.3 mg. for a 2-cm. cell, and 0.0025 to 0.05 mg. for a 10-cm. cell. Prepare a blank and a series of  $PO_4$  standards in 50.0 ml. volume with distilled water. Treat the blank and standards exactly as the sample throughout the procedure. Adjust the temperature of the blank, standards, sample, and reagents so that all are in the 20° to 30°C. range, and the variation is less than  $\pm 2^\circ C.$  among the entire set. Mixing after each addition, introduce 2.0 ml. ammonium molybdate reagent and 2.0 ml. aminonaphtholsulfonic acid reagent. After exactly 5 min., read the absorbance at 690  $m\mu$  preferably, or at 650  $m\mu$  in a spectrophotometer, or at 600 to 700  $m\mu$  in a filter photometer.

$$PO_4, \text{ milligrams per liter} = \frac{\text{milligrams of } PO_4 \times 1000}{\text{milliliters of sample}}$$

**Determination of Polyphosphate.**—Pipet into a beaker or flask 100 ml. clear and colorless sample, containing an amount of  $PO_4$  consistent with the color-developing procedure to be used subsequently. Add 1 to 2 drops phenolphthalein indicator and sufficient strong acid solution, dropwise, to discharge any resultant pink color. Then add 1.0 ml. in excess. Cover the beaker with a watch glass and boil gently for at least 90 min. Maintain the volume at 25 to 50 ml. distilled water. Alternatively, place in an autoclave or pressure cooker for 30 min. at 15 to 20 lb. per sq. in. Cool to room temperature, neutralize with 6  $N$  NaOH to a faint pink phenolphthalein color, and restore the original 100-ml. volume with distilled water. Develop the color and complete the determination by either the  $SnCl_2$  method or the aminonaphtholsulfonic acid method.

Polyphosphate, milligrams per liter

$$= \text{milligrams per liter of } PO_4 \text{ found after boiling} - \text{milligrams per liter of } PO_4 \text{ in original sample}$$

**Determination of Unfiltered Samples.**—When the  $PO_4$  and polyphosphate in the turbidity or settled precipitate of a sample must be ascertained, take two 100-ml. portions of the well-shaken unfiltered sample, and follow the procedures for  $PO_4$  and polyphosphate. Use the second portion as the photometric sample blank to which all reagents are added except the ammonium molybdate reagent. Substitute the strong acid solution for the molybdate in the blank.

Hydrochloric Acid, 1 *N*.

**Procedure. Total Alpha and Gross Beta Activity.**—Select a sample volume that will yield less than 200 mg. residue for  $\beta$  assay, and less than 100 mg. residue for  $\alpha$  assay for each 20 sq. cm. of counting pan area. Evaporate the sample to near dryness in a borosilicate-glass beaker or evaporating dish, after adding a few drops methyl orange indicator and sufficient 1 *N* HCl or 1 *N* HNO<sub>3</sub> to adjust the pH to 4 to 6. Do not bake the solids. Transfer the residue to a tared counting pan by means of a rubber policeman and distilled water from a wash bottle. Thoroughly cleanse the walls of the evaporating vessel with a few drops of acid and a rubber policeman, and add the acid washings to the counting pan. Avoid an excess of acid to reduce chemical attack of the aluminum counting pan. Dry the residue in an oven at 103° to 105°C., cool in a desiccator, weigh, and maintain in a dry condition until counting is finished. If the sample residue consists of light and easily air-borne particles, fix by treating with a few milligrams of lucite dissolved in acetone, air-dry, oven-dry, and weigh. Count the  $\alpha$  activity in an internal proportional counter at the  $\alpha$  plateau and the  $\beta$ - $\gamma$  activity at the  $\beta$  plateau.

**Alpha and Gross Beta Activity of Dissolved Matter.**—Filter the sample through a Gooch crucible, or a cellulose acetate membrane, if the suspended matter is to be examined. Follow the procedure for total  $\alpha$  and gross  $\beta$  activity. Record the pertinent activity and the method of filtration employed.

**Alpha and Gross Beta Activity of Suspended Matter.**—Three approaches are arranged in the order of preference: (a) select a sample volume that will yield less than 50 mg. suspended matter for  $\alpha$  examination, and less than 100 mg. for  $\beta$  examination for each 10 sq. cm. of membrane filter area. Under suction pass the sample through a cellulose acetate membrane filter, and wash the walls of the filter funnel with a few milliliters of distilled water. Oven-dry the filter on a tared counting pan, saturate the membrane with 95% ethyl alcohol, and ignite. After combustion ceases, fix the residue to the pan, and complete the ignition with a Meker burner. If the sample residue consists of light and easily air-borne particles, fix by treating with a few milligrams of lucite dissolved in acetone, air-dry, and count. Alternatively, handle the membrane filter by wetting the filter with conducting fluid, drying, weighing, and counting. In this case, include the weight of the membrane filter in the tare; (b) when highly polluted waters are difficult to filter through membrane filters, determine the total and dissolved activities, and calculate the activity due to suspended matter by difference; (c) filter the sample through an ashless mat or filter paper of stated porosity, dry, ignite, and weigh the suspended fixed residue. Transfer and fix a thin, uniform layer of sample residue to a tared counting pan by treating with a few milligrams of lucite in acetone. Dry, weigh, and count.

**Calibration of Over-All Efficiency of Internal Proportional Counter.**—Obtain a standard thallium-204 solution, which is certified by the National Bureau of Standards, and prepare with variable volumes of tap water a series of standards of known disintegration rate (1000 c.p.m.). When the tap water residue is low, add fine CaCO<sub>3</sub> powder to produce the variable residues up to 300 mg. in weight. Evaporate the standards to yield a series of uniformly deposited residues varying in thickness from 1 to 10 mg. per sq. cm. of bottom area in the counting pan. Upon drying at 103° to 105°C., weighing, and counting, calculate the ratio (efficiency) of counts per minute to disintegrations per minute for the different weights of residue. Use uranyl acetate as the  $\alpha$  calibration standard.

**Reporting of Results**—Report the  $\alpha$  or gross  $\beta$  activity in the sample and the counting error in terms of picocuries (pc) or nanocuries (nc) per liter of water

$$\text{Pc or nc per liter} = \frac{A \times 1000}{\text{milliliters of sample}}$$

where  $A$  =  $\alpha$  or gross  $\beta$  activity in terms of pc or nc

Disregard as insignificant that  $\alpha$  activity that is less than one half of the  $\beta$  counting error and report the gross  $\beta$  activity. When the  $\alpha$  activity in cpm exceeds one half the  $\beta$  error in cpm, subtract the net  $\alpha$  cpm from the net  $\beta$  cpm to obtain the net corrected  $\beta$  cpm. Then calculate and report the  $\beta$  activity in the usual manner as pc or nc per liter.

Include in the report the proper sample identifying data, sample volume, type of test, type of activity, type of counting equipment, standard calibration solutions used, counting time, weight of sample residue, and nature and amount of radio activity.

### RESIDUAL (SOLIDS) <sup>2-11</sup>

Residue dried at 103° to 105°C often contains some occluded water. Drying at 179° to 181°C usually removes most of the occluded water, converts the bicarbonate to carbonate more completely and may result in the loss of some chloride and nitrate salts. The total residue at 179° to 181°C generally agrees more closely with the values obtained by the summation of the individually determined mineral salts. Water samples having an appreciable organic matter content or with a pH in excess of 9.0 are best dried at 179° to 181°C.

A platinum dish and a Gooch crucible are desirable for the determination of fixed residues at 600°C. In the temperature range between 100°C and 185°C however, evaporating dishes can be constructed of nickel porcelain and silica or borosilicate glass. The same applies to the filtering materials. Diatomaceous filter candles, filter paper, and cellulose acetate membrane filters, as well as silica fritted glass porcelain stainless steel and alundum filters can be used in the 100° to 185°C range.

**Procedure** **Total Residue**—Pipet into an ignited and weighed platinum evaporating dish a volume of well mixed sample that will yield between 25 and 250 mg residue. Evaporate the sample to dryness on a steam bath, and dry to constant weight in an oven adjusted at either 103° to 105°C or 179° to 181°C. Weigh the dish immediately after cooling to room temperature in a desiccator.

**Fixed Residue**—Ignite the residue at 600°C for 1 hr, and weigh the dish immediately after cooling to room temperature in a desiccator.

**Filtrable and Nonfiltrable Residue**.—Ignite a prepared Gooch crucible at 600°C for at least 30 min and weigh immediately after cooling to room temperature in a desiccator. Mix well the suspended matter in the sample, and filter a suitable volume. Transfer the filtrate to an ignited and weighed, platinum evaporating dish, and evaporate to dryness on a steam bath if the filtrable residue is desired. Dry both the filtrable and nonfiltrable residue to constant weight in an oven adjusted at either 103° to 105°C or 179° to 181°C. Weigh the dish or crucible immediately after cooling to room temperature in a desiccator.

**Fixed Residue**—Ignite the filtrable and/or nonfiltrable residue at 600°C for 1 hr, and weigh the dish immediately after cooling to room temperature in a desiccator.



Record the residue to 3 significant figures and state the drying temperature used

$$\text{Residue, milligrams per liter} = \frac{\text{milligrams of residue} \times 1000}{\text{milliliters of sample}}$$

## SELENIUM

### *DISTILLATION AND SOL METHOD*<sup>2</sup>

Color reproducibility of the red sol in the visual color matching method is best insured by subjecting the sample and Se standards to the same treatment throughout the distillation and color development procedure

**Reagents for Distillation.** Standard Selenium Solution.—(a) Dissolve 0.1000 g pure Se metal by warming with 5 ml concentrated  $\text{HNO}_3$ , cautiously evaporating just to dryness, and diluting to 1000 ml with distilled water. (b) Dilute 10.00 ml stock solution to 100 ml with distilled water to give a standard solution containing 0.010 mg Se per 100 ml. Prepare the standard solution daily.

Sulfuric-Nitric Acid Solution.—One volume concentrated  $\text{H}_2\text{SO}_4$  + 2 volumes concentrated  $\text{HNO}_3$ .

Hydrobromic Acid-Bromine Reagent.—Fifteen ml liquid bromine + 985 ml 48% HBr.

Sulfuric Acid, Concentrated.

Sodium Peroxide.

**Reagents for Visual Color Comparison.** Gum Arabic (Gum Acacia) Reagent, 5 g. per 100 ml.—Filter through a glass wool mat, and prepare daily.

Sulfur Dioxide Gas.

Hydroxylamine Hydrochloride.

**Procedure.**—Select a sample volume (1 to 10 l) containing 0.01 to 0.10 mg Se. Make the sample alkaline with fresh  $\text{Na}_2\text{O}_2$  and evaporate to 100 ml. Add fresh  $\text{Na}_2\text{O}_2$  as needed to keep the sample alkaline throughout the concentration process. Evaporate the final 100 ml nearly to dryness over a steam or water bath. Oxidize any organic matter with a few drops  $\text{H}_2\text{SO}_4$   $\text{HNO}_3$  solution.

**Distillation.**—Conduct the entire distillation in an efficient fuming hood because of the copious evolution of bromine fumes. Steam out the borosilicate glass distillation apparatus illustrated in Fig. 48.6 (p. 2432). Transfer the concentrate and residue to the 500 ml distilling flask. Add to the evaporating vessel a volume of concentrated  $\text{H}_2\text{SO}_4$  equal to the volume of the transferred concentrate, and again rub down the sides with a policeman to remove the clinging residue. Transfer the  $\text{H}_2\text{SO}_4$  to the distilling flask. Rinse the evaporating vessel with alternate 25 ml portions of distilled water and concentrated  $\text{H}_2\text{SO}_4$ . Restrict the total volume of water used, including the concentrate, to 50 to 75 ml. Mark off a circle at the 85 ml liquid level on a 100 ml beaker or other suitable receiver, and tip the beaker containing 10 ml distilled water so that the delivery end of the vertical condenser is below the water surface. Introduce 60 ml HBr-bromine reagent into the distilling flask, replace the glass stopper, and regulate the heating rate so that 75 ml distillate will be recovered after 30 min distillation.

Prepare a series of Se standards in the 0 to 0.100 mg range so that 50 ml of the total volume of 100 ml will be composed of concentrated  $\text{H}_2\text{SO}_4$ . Place each standard in the distilling flask, add 60 ml HBr-bromine reagent, and distill in the same manner as the sample.

**Color Comparison**—Attach a 1 ml measuring pipet by means of a 2 ft length of rubber tubing to the needle valve of a cylinder of  $\text{SO}_2$  gas and adjust the gas bubbling rate to about 5 bubbles per second in a beaker of distilled water. Place the gas admitting pipet in each beaker of distillate and stir with the pipet until the bromine color disappears and for 5 sec thereafter. Mixing after each addition add 1 ml gum arabic reagent and 0.5 g  $\text{NH}_4\text{OH} \cdot \text{HCl}$ . After 1 hr transfer to 100 ml tall form Nessler tubes for visual color comparison.

$$\text{Se, milligrams per liter} = \frac{A \times 1000}{\text{milliliters of sample}} \times \frac{B}{C}$$

where  $A$  = milligrams of Se found visually. The ratio  $B/C$  applies only when a sample is distilled the volume then made up to  $B$  and aliquot  $C$  taken from it for color development.

### DIAMINOBENZIDINE METHOD<sup>52</sup>

The diaminobenzidine photometric method is sufficiently sensitive and specific to enable the use of smaller samples than the distillation-sol method. Iodide and to a lesser extent bromide cause low selenium results.

**Reagents** Standard Selenium Solution—Prepare as described in the distillation-sol method.

**3,3-Diaminobenzidine Hydrochloride Solution** 10 mg per milliliter—Prepare only sufficient reagent for one day's requirements because of instability and expense.

**Calcium Chloride Solution**—Three g  $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$  in 100 ml distilled water.

**Ammonium Chloride Solution** Twenty-five g in 100 ml distilled water.

**EDTA Sodium Sulfate Reagent** Dissolve 10 g disodium ethylenediaminetetraacetate dihydrate and 20 g  $\text{Na}_2\text{SO}_4$  in 100 ml distilled water. Add concentrated  $\text{NH}_4\text{OH}$  dropwise with stirring until dissolution is complete.

**Ammonium Hydroxide** 5 N 1 + 2

**Methyl Orange Indicator**

**Hydrochloric Acid** Concentrated

**Hydrochloric Acid** 0.1 N

**Sodium Hydroxide** 0.1 N

**Potassium Permanganate** 0.1 N

**Sodium Sulfate**

**Toluene**

**Procedure**—Select a sample volume containing less than 0.05 mg Se. For most purposes a 1000 ml sample is adequate. Place the sample in a 2 l beaker, add 10 drops methyl orange indicator solution and titrate to the methyl orange end point with 0.1 N  $\text{HCl}$ , then add 2 ml excess. Add 3 drops 0.1 N  $\text{KMnO}_4$ , 5 ml  $\text{CaCl}_2$  solution and several glass beads to prevent bumping. Boil the volume down to 250 ml, adding  $\text{KMnO}_4$  as required to maintain a purple tint. Then transfer the solution to a 500 ml flask. Ignore any  $\text{MnO}_2$  precipitate that may form as it has no adverse effect.

Prepare a blank and a series of Se standards (0.010, 0.025 and 0.050 mg) and bring their volume to 250 ml in a 500 ml flask. Add 10 drops methyl orange indicator solution, 2 ml 0.1 N  $\text{HCl}$ , 5 ml  $\text{CaCl}_2$  solution, 3 drops 0.1 N  $\text{KMnO}_4$ .

and several glass beads. Treat the blank and standards exactly as the sample throughout the rest of the procedure.

Heat to boiling, and add more  $\text{KMnO}_4$  as needed to maintain a slight purple color. Boil vigorously to expel  $\text{CO}_2$ . After 5 min. of boiling, add 5 ml. 0.1  $N$   $\text{NaOH}$ . When the volume has decreased to 25 ml., complete the evaporation to dryness cautiously. Avoid prolonged heating of the residue at temperatures substantially over  $100^\circ\text{C}$ . Cool the flask, add 10 ml.  $\text{NH}_4\text{Cl}$  solution and 5 ml. concentrated  $\text{HCl}$ . Float the flask on about 900 ml. gently boiling water in a 1-liter beaker for  $10 \pm 0.5$  min. Transfer the solution and  $\text{NH}_4\text{Cl}$  precipitate, if present, from the flask to a 250-ml. beaker, rinsing the flask with 5 ml.  $\text{EDTA-Na}_2\text{SO}_4$  reagent and 5 ml. 5  $N$   $\text{NH}_4\text{OH}$ . Using a pH meter, adjust the pH to  $1.5 \pm 0.3$  with 5  $N$   $\text{NH}_4\text{OH}$ . Ignore the precipitate of  $\text{EDTA}$  that may form at this stage. Add 1 ml. 3,3'-diaminobenzidine hydrochloride solution, and float the beaker on about 200 ml. gently boiling water in a 400-ml. beaker for about 5 min. Cool, and, using a pH meter, add 5  $N$   $\text{NH}_4\text{OH}$  to adjust the pH to  $8 \pm 1$ . (The  $\text{EDTA}$  precipitate will redissolve at this point.) Transfer the solution to a 50-ml. graduated cylinder, and adjust the volume to  $50 \pm 1$  ml. with washings from the beaker. Pour the contents of the graduate into a 250-ml. separatory funnel, add 10 ml. toluene, and shake for  $30 \pm 5$  sec. Discard the aqueous layer, transfer the organic phase to a 12 to 15 ml. centrifuge tube, and centrifuge briefly to clear the toluene of water droplets. In the absence of a centrifuge, filter the organic phase through a dry filter paper, on which has been placed 0.1 g.  $\text{Na}_2\text{SO}_4$ . Read the absorbance at  $420 \text{ m}\mu$  in a 1-cm. cell against a reference of pure toluene.

$$\text{Se, milligrams per liter} = \frac{\text{milligrams of Se} \times 1000}{\text{milliliters of sample}}$$

## SILICA

The gravimetric method finds greatest application in the  $\text{SiO}_2$  range above 20 mg. per liter, and enables the standardization of the standard  $\text{Na}_2\text{SiO}_3$  solution used in the colorimetric methods. The heteropoly blue colorimetric method is adaptable for the lowest  $\text{SiO}_2$  range of 0.04 to 2 mg. per liter, whereas the yellow molybdosilicate colorimetric method is suitable in the intermediate range of 1 to 25 mg. per liter. Reagent blanks are mandatory in all 3 methods.

Chemicals low in  $\text{SiO}_2$  should be reserved for both the gravimetric and colorimetric methods in order to minimize reagent blanks. Distilled water, reagents, and samples should be stored in plastic containers to avert  $\text{SiO}_2$  pick-up.

### GRAVIMETRIC METHOD<sup>2,11</sup>

*Reagents.* Hydrochloric Acid, Concentrated.

Sulfuric Acid, Concentrated.

Hydrofluoric Acid, 48%.

Hydrochloric Acid, 1 + 50.

*Procedure.*—Select a sample volume (1000 ml. or more) containing at least 10 mg.  $\text{SiO}_2$  and preferably in excess of 100 mg. If necessary, clarify the sample by filtration. Acidify with 2 to 3 ml. concentrated  $\text{HCl}$ , and evaporate to dryness in a 200-ml. platinum dish on a steam or water bath. At regular intervals apply 2 or more portions of 2 to 3 ml. concentrated  $\text{HCl}$ , as additional increments of sample are transferred to the dish. Bake the evaporated residue in an oven at  $110^\circ\text{C}$ . for

30 to 60 min. Add 5 ml concentrated HCl to the dried residue, warm on the steam bath and follow with 50 ml hot distilled water. Loosen the clinging residue from the sides and bottom of the dish with a rubber policeman and collect the hot precipitate on an ashless medium textured filter paper. Save the filtrate and washings. Wash the dish and residue with hot 1 + 50 HCl and finally with several small increments of distilled water until the washings are chloride free. Save the filter paper for subsequent ignition. Return the filtrate and washings to the platinum dish and again evaporate to dryness. Bake the evaporated residue in an oven at 110°C for 30 to 60 min. Repeat the filtration and washing steps but with a separate filter paper. If desired retain the filtrate and washings for the oxalate methods for Ca and the gravimetric determination of Mg or SO<sub>4</sub>. Carefully char the 2 filter papers in a platinum crucible that has previously been ignited and weighed. Burn off the final traces of paper without causing a flame and ignite at 1000° to 1200°C for 30 min. or to constant weight. Cool the crucible in a desiccator and weigh. Moisten the residue in the crucible with a few drops of distilled water, add 2 drops concentrated H<sub>2</sub>SO<sub>4</sub> and 10 ml 48% HF. Cautiously evaporate to dryness on a low temperature hot plate or on a steam bath in a hood. Again ignite the residue to constant weight at 1000° to 1200°C. Cool the crucible in a desiccator and weigh. Carry a blank through the entire procedure to correct for the SiO<sub>2</sub> contributed by the reagents and apparatus.

$$\text{SiO}_2 \text{ milligrams per liter} = \frac{(A - B) - (C - D)}{\text{milliliters of sample}} \times 1000$$

where *A* = weight of crucible and sample residue, in milligrams, after first ignition,  
*B* = weight of crucible and sample residue, in milligrams, after HF treatment and second ignition,  
*C* = weight of crucible and blank residue, in milligrams, after first ignition and  
*D* = weight of crucible and blank residue, in milligrams, after HF treatment and second ignition

#### COLORIMETRIC METHODS<sup>2, 11</sup>

Preliminary sample digestion with NaHCO<sub>3</sub> is designed to increase the SiO<sub>2</sub> available for reaction with the molybdate reagent. When reliance is placed on NaHCO<sub>3</sub> the result is reported as total dissolved SiO<sub>2</sub> colorimetric. In the absence of NaHCO<sub>3</sub> treatment, the result is designated as molybdate reactive dissolved SiO<sub>2</sub>.

Chromate and large amounts of Fe, PO<sub>4</sub>, sulfide, tannin, color and turbidity are potential interferences. Oxalic acid treatment suppresses PO<sub>4</sub> and reduces tannin interference. Inorganic sulfide can be removed by boiling an acidified sample. The addition of 1 ml disodium ethylenediaminetetraacetate dihydrate (1 g per 100 ml) after the molybdate reagent overcomes high Fe and Ca concentrations.

**Reagents** Standard Silica Solution—(a) Dissolve 4.732 g Na<sub>2</sub>SiO<sub>3</sub> · 9H<sub>2</sub>O in boiled and cooled distilled water and dilute to 900 ml. Check the concentration of 100.0-ml aliquots by the gravimetric method and adjust the stock solution to 100 mg SiO<sub>2</sub> per 100 ml. (b) Dilute 10.00 ml stock solution to 1000 ml with boiled and cooled distilled water to form a standard solution containing 0.010 mg SiO<sub>2</sub> per 100 ml.

Ammonium Molybdate Solution, 10 g.  $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$  per 100 ml.—Filter if necessary.

Oxalic Acid Solution, 10 g.  $\text{C}_2\text{H}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$  per 100 ml.

Sulfuric Acid, 1 N.

Hydrochloric Acid, 1 + 1.

Sodium Bicarbonate (Silica-Free).

*Reagents for Permanent Color Standards in Molybdosilicate Method.* Potassium Chromate Solution, 0.63 g.  $\text{K}_2\text{CrO}_4$  per liter. When each 1.0 ml. of this solution is diluted to 30 ml. with distilled water, and then mixed with 25 ml. borax solution, the resulting permanent color standard is equivalent to an increment of 0.10 mg. in the range 0.10 to 1.0 mg.  $\text{SiO}_2$ .

Borax Solution, 10 g.  $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$  per liter.

*Reagents for Heteropoly Blue Method.* Reducing Agent.—(a) Dissolve 0.5 g. 1-amino-2-naphthol-4-sulfonic acid (use a powder no darker than a pale pink in color) and 1 g.  $\text{Na}_2\text{SO}_3$  in 50 ml. distilled water. (b) Dissolve 30 g.  $\text{NaHSO}_3$  in 150 ml. distilled water. (c) Add solution (a) to solution (b), and filter if necessary. Store in a refrigerator or out of the light. Discard when the solution darkens.

*Procedure.* Preliminary Treatment of Sample.—If necessary, clarify the sample by centrifuging or by filtration. Select a sample volume containing less than 1.0 mg.  $\text{SiO}_2$  if the molybdosilicate method is used, and 0.30 mg. if the heteropoly blue method is used. Pipet into a platinum dish, and dilute, if necessary, to 50 ml. with distilled water. Digest with 0.20 g.  $\text{NaHCO}_3$  for 1 hr. on a steam or water bath. Cool to room temperature and neutralize with 2.4 ml. 1 N  $\text{H}_2\text{SO}_4$ . Complete the determination without pausing at this stage. Transfer the solution to a 50-ml. Nessler tube, and dilute to the mark with distilled water. Develop the color by either the molybdosilicate method or the heteropoly blue method.

*Preparation of Silica Standards.*—For the photometric molybdosilicate method, prepare a series of calibration standards in 50.0 ml. volume in the range 0.200 to 1.30 mg.  $\text{SiO}_2$  for absorbance measurements at 410  $m\mu$  in a 1-cm. cell, and 0.040 to 0.250 mg.  $\text{SiO}_2$  for a 5-cm. cell. Add 0.20 g.  $\text{NaHCO}_3$  and 2.4 ml. 1 N  $\text{H}_2\text{SO}_4$  to each standard.

For the visual molybdosilicate method, prepare the following series of permanent color standards by measuring from a buret 0, 1.0, 2.0, 4.0, 5.0, 7.5, and 10.0 ml.  $\text{K}_2\text{CrO}_4$  solution into 50-ml., tall-form Nessler tubes. Dilute with distilled water to a 30-ml. volume, add 25 ml. borax solution, and mix. Modify and adjust the tints of these permanent standards as necessary by checking with the color developed in comparable  $\text{SiO}_2$  standards. Recheck and readjust the permanent standards every time a new batch of ammonium molybdate and oxalic acid solution is prepared.

For the photometric heteropoly blue method, prepare a series of calibration standards in 50.0 ml. volume in the range 0.040 to 0.300 mg.  $\text{SiO}_2$  for absorbance measurements at 650  $m\mu$  in a 1-cm. cell, and 0.007 to 0.050 mg.  $\text{SiO}_2$  for a 5-cm. cell. At 815  $m\mu$ , substitute the  $\text{SiO}_2$  ranges of 0.020 to 0.100 mg. and 0.004 to 0.020 mg. respectively. Add 0.20 g.  $\text{NaHCO}_3$  and 2.4 ml. 1 N  $\text{H}_2\text{SO}_4$  to each standard.

For the visual heteropoly blue method, prepare a series of 12 equally spaced, temporary standards in 50-ml. Nessler tubes in the range 0 to 0.12 mg.  $\text{SiO}_2$ .

*Color Development.*—To the blank, temporary or calibration standards, and sample add in rapid succession 1.0 ml. 1 + 1 HCl and 2.0 ml. ammonium molybdate

inadequately rinsed apparatus. Standard solutions and samples should preferably be stored in polyethylene bottles to minimize contamination, or, secondarily, in borosilicate glassware.

**Reagents.** Deionized Distilled Water.—This should be used in the preparation of all solutions and dilutions.

**Standard Sodium Solution.**—(a) Dissolve 2.542 g. NaCl, dried at 140°C., and dilute to 1000 ml. with water to form a solution containing 1.00 mg. Na per 1.00 ml. Use this solution for preparing the calibration curve in the Na range 10 to 100 mg. per liter. (b) Dilute 10.00 ml. stock solution to 100 ml. to form an intermediate dilution containing 0.100 mg. Na per 1.00 ml. Use this solution for preparing the calibration curve in the Na range 1 to 10 mg. per liter. (c) Dilute 10.00 ml. intermediate dilution to 100 ml. to form a standard solution containing 0.010 mg. Na per 1.00 ml. Use this solution for preparing the calibration curve in the Na range 0.1 to 1.0 mg. per liter.

**Reagents for Internal-Standard Method.** **Standard Lithium Solution.**—Dissolve 49.67 g.  $\text{LiNO}_3$ , dried at 105°C. to constant weight, and dilute to 1000 ml. with water to form a solution containing approximately 5.0 mg. Li per 1.00 ml. Recalibrate the instrument whenever a new batch of this solution is prepared.

**Procedure.**—The differences among the makes and models of satisfactory flame photometers render impossible the formulation of detailed instructions applicable to every instrument. On this account, the manufacturer's recommendations must be followed for the selection of the proper photocell and wavelength, the adjustment of the slit width and sensitivity, the appropriate fuel and air or oxygen pressures, and the steps for warm-up, ignition of sample, and measurement of the emission intensity.

**Direct-Intensity Method.**<sup>11</sup>—Prepare 11 Na standards in each of the following ranges: 0 to 1, 0 to 10, and 0 to 100 mg. per liter. Space the standards at intervals of one-tenth of the maximum concentration in each Na range. Starting with the highest standard and working toward the most dilute, measure the emission intensity at 589  $\mu$ . Construct a calibration curve by plotting the emission intensity (scale reading) versus concentration on linear graph paper. Record such pertinent data as the slit width, and fuel and air or oxygen pressures used in the particular Na range.

Remove any burner-clogging suspended matter from the sample by filtration through an 11-cm. ashless filter paper of medium retentiveness, first making certain that the paper is Na- and K-free. Determine the emission intensity of the sample at the wavelength, slit width, and fuel and air or oxygen pressures used in the preparation of the calibration curve. From the curve, select and prepare the Na standards that immediately bracket the emission intensity of the sample. Determine the emission intensities of the bracketing standards (one Na standard slightly less and the other slightly greater than the sample) and the sample as nearly simultaneously as possible. Repeat the determination on both the bracketing standards and the sample. Calculate the Na concentration by the equation presented below, and average the 2 or more findings for a final result.

**Internal-Standard Method.**<sup>11</sup>—Follow the procedure described in the direct-intensity method with the following exceptions: prepare the Na standards in 50.0 ml. volume, then add with a volumetric pipet 5 ml. standard Li solution; construct the calibration curve by plotting the average emission intensity (average scale reading) versus Na concentration on linear graph paper; record such pertinent data as the gain settings, null point, and fuel and air or oxygen pressures

used in each Na range, into each 500 ml sample (filtered if necessary), or aliquot diluted to 500 ml, pipet 5 ml standard Li solution

$$\text{Na, milligrams per liter} = \left[ \frac{(A - B)(c - b)}{(a - b)} + B \right] \times D$$

where  $A$  = milligrams per liter of Na concentration of the upper bracketing standard,

$B$  = milligrams per liter of Na concentration of the lower bracketing standard,

$a$  = emission intensity of the upper bracketing standard,

$b$  = emission intensity of the lower bracketing standard,

$c$  = emission intensity of the sample, and

$D$  = dilution ratio

$$= \frac{\text{milliliters of sample volume} + \text{milliliters of distilled water volume}}{\text{milliliters of sample volume}}$$

### GRAVIMETRIC METHOD<sup>2</sup> 11, 17, 53

The appreciable solubility of sodium zinc uranyl acetate hexahydrate in water places a premium on good technique throughout the procedure. Lithium should be absent while  $k$  must be limited to a concentration of 25 mg in the 1 ml reconstituted solution. Since  $\text{K}_2\text{SO}_4$  is only slightly soluble in the zinc uranyl acetate reagent,  $\text{SO}_4$  should not be present concurrently with considerable amounts of  $k$ . Organic acids such as oxalic, citric, and tartaric can also interfere. Phosphate and  $\text{SiO}_2$  interference can be deducted after the sodium zinc uranyl acetate precipitate has been dissolved and removed with warm distilled water in the final steps of the procedure.

**Reagents.** Zinc Uranyl Acetate Reagent—Mix 27 ml glacial acetic acid with 100 ml distilled water. Add 10 g  $\text{UO}_2(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot 2\text{H}_2\text{O}$  and 30 g  $\text{Zn}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot 2\text{H}_2\text{O}$  to the solution and warm to dissolve. On cooling, add 2 to 3 mg NaCl and filter the reagent after 24 hr, or just before use. Store in a borosilicate-glass bottle.

**Ethyl Alcohol Wash Solution**—Saturate 95% ethyl alcohol with pure sodium zinc uranyl acetate, and decant or filter the solution just prior to use. Prepare the sodium zinc uranyl acetate by adding 25 ml zinc uranyl acetate reagent to 2 ml NaCl solution (10 mg NaCl), stirring, collecting the precipitate in a sintered glass crucible, and washing 3 times with glacial acetic acid, and finally 3 times with ethyl ether.

**Ethyl Ether.**

**Procedure.**—If necessary, remove any suspended matter from the sample by filtration. Select a sample volume containing less than 8 mg Na and less than 25 mg  $k$ . Pipet the clear sample into a 20 or 50 ml borosilicate glass beaker and evaporate to dryness on a steam or water bath. Cool the residue to room temperature, add 10 distilled water, and rub with a stirring rod. If the residue fails to dissolve, add more 10 ml increments of distilled water to put the residue into solution. Ignore a feathery turbidity of  $\text{CaSO}_4$  at this point because of its subsequent solubility in the zinc uranyl acetate reagent. Treat with zinc uranyl acetate reagent in the ratio of 10 ml reagent for each 10 ml increment of distilled water required to dissolve the residue. Mix, cover the beaker, and allow to stand for 1 hr. Stir periodically to prevent the formation of a supersaturated solution. Collect the precipitate under suction in a weighed, medium porosity, sintered glass

<sup>53</sup> Barber, H. H., and Kolthoff, I. M., *J. Am. Chem. Soc.*, 50, 1623, 1928, 51, 3233, 1929

crucible. Substitute a porous-bottomed porcelain filtering crucible if desired. Drain the filter as dry as possible under suction. Wash the beaker, crucible, and precipitate 5 to 8 times with 2-ml. portions zinc uranyl acetate reagent. Drain the crucible completely after the last wash in order to remove traces of the zinc uranyl acetate reagent. Next wash 5 times with 2-ml. portions ethyl alcohol wash solution. Conclude the washing with 3 small portions ethyl ether. Continue the suction for a few minutes until the ethyl ether is volatilized and the precipitate is dry. Wipe the outside and inner bottom ring of the crucible with a cloth if salts have crystallized there. Transfer the crucible to the balance case, and weigh after 10 to 15 min., and again 10 min. later to check on the constancy of the weight. Return the crucible to the suction apparatus and dissolve the sodium zinc uranyl acetate by passing 100 ml. warm distilled water in small portions through the filter. Dry the crucible with ethyl alcohol wash solution and ethyl ether as previously directed, and reweigh. The difference in the weight before and after the distilled water treatment represents the weight of the sodium zinc uranyl acetate.

$$\text{Na, milligrams per liter} = \frac{\text{milligrams of sodium zinc uranyl acetate} \times 14.95}{\text{milliliters of sample}}$$

### STRONTIUM<sup>2, 54</sup>

The entire section above, on the flame photometric method under "Sodium," should be examined for the general factors affecting a typical flame photometric determination. The standard addition method described for Sr distributes the same ions throughout the standards and sample, thus equalizing the radiation effect of possible interfering substances in both standards and sample. The background emission intensities at wavelengths 454 and 460.7  $\mu$  are the same, thereby enabling the first wavelength to be reserved for background measurement and the second for Sr measurement.

Polyethylene bottles are preferred for storage of samples and standards, although borosilicate glassware may be used.

**Reagents.** **Standard Strontium Solution.**—(a) Suspend 1.685 g.  $\text{SrCO}_3$ , dried overnight at 105°C., in 200 ml. distilled water contained in a 1-liter, borosilicate-glass, volumetric flask. Through a funnel, carefully add small amounts 1 + 1 HCl, until all the  $\text{SrCO}_3$  dissolves. Guard against the loss of  $\text{SrCO}_3$  due to vigorous and uncontrolled effervescence. After the  $\text{SrCO}_3$  has dissolved, boil off the  $\text{CO}_2$  for a few minutes, cool, and neutralize the solution to methyl red indicator with 3 *N*  $\text{NH}_4\text{OH}$ . Dilute to the mark with distilled water to form a solution containing 1.00 mg. Sr per 1.00 ml. (b) Dilute 25.00 ml. stock solution to 1000 ml. to form a standard solution containing 0.025 mg. Sr per 1.00 ml. Use this standard solution for preparing the calibration curve in the Sr range 1 to 25 mg. per liter.

**Nitric Acid, Concentrated.**

**Procedure.**—Select a sample volume containing less than 1 mg. Sr. Concentrate a sample having less than 2 mg. per liter of Sr by adding 0.15 to 0.20 ml. concentrated  $\text{HNO}_3$  to 250 ml. (or more) sample, and evaporating to 25 ml. Use concentrated  $\text{HNO}_3$  sparingly to avoid interference. Transfer the cooled concentrate to a 50-ml. volumetric flask, and dilute to the mark.

Prepare Sr standards of 0, 2.0, 5.0, and 10.0 mg. per liter if a natural water is being examined, and 0, 25, 50, and 75 mg. per liter for a brine. (If necessary, dilute the brine sufficiently to prevent burner splatter and clogging.) In a 50-ml.

<sup>54</sup> Chow, T. J., and Thompson, T. G., *Anal. Chem.*, **27**, 18, 1955.



volumetric flask mix 25.0 ml sample or concentrate, containing less than 10 mg Ca or Ba, with 25.0 ml of each of the Sr standards

Determine the emission intensities of the sample and standards at wavelengths 460.7 and 454 m $\mu$ . Follow the manufacturer's instructions for the operation of the flame spectrophotometer equipped with a photomultiplier tube (Beckman Model DU or equivalent)

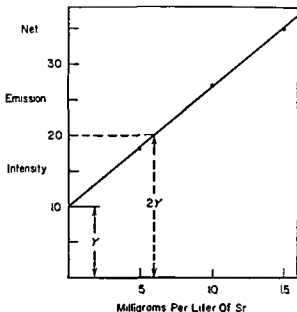


Fig 48.8 Graphical Calculation of Strontium Concentration

Plot the net emission (intensity reading at 460.7 m $\mu$  minus the background radiation reading at 454 m $\mu$ ) versus the Sr concentration that was added to the sample or concentrate. Inasmuch as the plot forms a straight calibration line that intersects the ordinate, compute the Sr concentration by the following equation

$$\text{Sr, milligrams per liter} = \frac{A - B}{C} \times \frac{D}{E}$$

where  $A$  = sample emission intensity reading at 460.7 m $\mu$ ,  
 $B$  = background radiation reading at 454 m $\mu$ , and  
 $C$  = slope of calibration line

The ratio  $\frac{D}{E}$  applies only when  $E$  milliliters of sample is evaporated to form a concentrate of 25.0 ml, the value for  $D$

Alternatively, calculate the Sr concentration by the graphical method shown in Fig 48.8<sup>55</sup>. Since the calibration line intersects the ordinate at 10,  $y = 10$ , and  $2y = 20$ . The point on the abscissa corresponding to the ordinate value of 20 is 6.0 mg per liter of Sr

<sup>55</sup> Reproduced with permission from *Standard Methods for the Examination of Water and Wastewater*, 11th Ed. The American Public Health Assn., Inc., New York, 1960

SULFATE <sup>2,11</sup>

The classical gravimetric method for  $\text{SO}_4$  is acknowledged to yield the most reliable results in the concentration range above 10 mg. per liter. The turbidimetric method is sufficiently precise, rapid, and simple for routine use in the  $\text{SO}_4$  range 5 to 60 mg. per liter.

Sulfate samples should be refrigerated or dosed with formaldehyde to inhibit microbiological reduction to sulfide. The pH of samples containing sulfite should be lowered below 8.0 in order to retard atmospheric oxidation to  $\text{SO}_4$ .

## GRAVIMETRIC METHOD

Coprecipitation with  $\text{BaSO}_4$  is a common phenomenon that is affected by the amount and nature of the associated cations and anions. Small quantities of ferrous, Mg, Zn, and Al may be tolerated. Ferric, Ca, and  $\text{NO}_3$  may exert an adverse effect in appreciable quantity. Turbidity and  $\text{SiO}_2$  should be removed before the  $\text{SO}_4$  is precipitated. Because positive errors may result from the oxidation of sulfite and sulfide to  $\text{SO}_4$  during the procedure, a correction for sulfite should be applied by a preliminary estimate and oxidation to  $\text{SO}_4$ .

*Reagents.* Barium Chloride Solution.—Ten g.  $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$  per 100 ml.

Methyl Red Indicator.

Hydrochloric Acid, 1 + 1.

*Procedure.*—Remove the  $\text{SiO}_2$  and suspended matter as described in "Gravimetric Method," under "Silica," p. 2475, above.

Dilute or concentrate the filtrate from the  $\text{SiO}_2$  determination to a convenient volume.

*Precipitation of Sulfate.*—Select an aliquot containing approximately 50 mg.  $\text{SO}_4$ , and bring the total volume to 250 ml. If the  $\text{SO}_4$  concentration is below 50 mg., concentrate the total volume to 150 ml. Acidify the solution with 1 + 1 HCl to the pink color of methyl red indicator, heat to boiling, and add warm  $\text{BaCl}_2$  solution dropwise with constant stirring, until precipitation seems to be complete. Then add 2 ml. in excess. In the presence of a small amount of precipitate use a total of 5 ml.  $\text{BaCl}_2$  solution; for most other situations 10 ml. will suffice. Cover the beaker with a watch glass and digest at  $80^\circ$  to  $90^\circ\text{C}$ . for at least 2 hr., and preferably overnight. Add a small quantity of ashless filter paper pulp and at room temperature collect the precipitate on any one of the following filters: an ashless, fine textured, retentive filter paper; or a Gooch, silica, or porcelain crucible that has previously been prepared, ignited, and weighed. Wash the beaker and precipitate several times with small portions of warm distilled water until the washing becomes free of Cl. If a filter paper is used, carefully char in a crucible that has previously been ignited and weighed, and burn off the final traces of paper without causing a flame. Dry the other filters containing the precipitate. Ignite all crucibles at  $800^\circ\text{C}$ . for 30 to 60 min. or to constant weight. Cool the crucible in a desiccator and weigh the  $\text{BaSO}_4$  precipitate.

$$\text{SO}_4, \text{ milligrams per liter} = \frac{\text{milligrams of BaSO}_4 \times 411.5}{\text{milliliters of sample}}$$

## TURBIDIMETRIC METHOD

For best results, the experimental conditions involving temperature, measurement of  $\text{BaCl}_2$  crystals, mixing, and standing time should be kept as constant as

**Reagents.** Boiled Distilled Water.—This should be used for the preparation of all solutions and dilutions.

**Standard Sodium Thiosulfate Titrant, 0.025 N.**—Prepare and standardize as described under "Dissolved Oxygen," p. 2457, above. The equivalence of 0.02500 N  $\text{Na}_2\text{S}_2\text{O}_3$  is 0.400 mg. S per 1.00 ml.

**Standard Iodine Solution, 0.025 N.**—Dissolve 20 to 25 g. KI in 50 ml. distilled water, and add 3.175 g. resublimed iodine with stirring. When dissolution is complete, dilute to 1 liter, and store in a cool, dark place. Standardize daily against standard 0.025 N  $\text{Na}_2\text{S}_2\text{O}_3$  titrant, using approximately the same volumes of concentrated HCl, water, and starch indicator as in the actual sample titration. The equivalence of 0.02500 N iodine is 0.400 mg. S per 1.00 ml.

Sulfuric Acid, Concentrated.

Hydrochloric Acid, Concentrated.

Carbon Dioxide Gas.

Zinc Acetate Solution, 1 M, 22.0 g.  $\text{Zn}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot 2\text{H}_2\text{O}$  per 100 ml.

Starch Indicator.

**Reagents for Dissolved Sulfide.** Coagulant Solution.—One hundred g.  $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$  or  $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$  + 144 ml. distilled water. Filter if necessary.

Sodium Hydroxide, 6 N.

**Procedure.** Total Sulfide.—Use either a 1-liter aeration cylinder equipped with an aluminum filter disc at the bottom, or a 1-liter, wide-mouthed bottle, surmounted with a 2-hole stopper, holding a fritted-glass diffuser tube and an outlet tube. Connect the outlet tube to a 10-bulb absorption tube or two 125-ml. conical flasks, with suitable connections to admit gas through the flasks in series. Pass  $\text{CO}_2$  or other inert gas from a cylinder or a generator through the apparatus to displace the air, before introducing the sample and acidifying.

Place 500 ml. of the specially collected sample (or an aliquot containing 0.5 to 10 mg. sulfide) in the 1-liter aeration cylinder or wide-mouthed bottle, and 5 ml.  $\text{Zn}(\text{C}_2\text{H}_3\text{O}_2)_2$  solution and 95 ml. distilled water in the absorption tube or each of the 2 conical flasks. Acidify the sample with 10 ml. concentrated  $\text{H}_2\text{SO}_4$ , and for 1 hr., sweep all the sulfide from the sample into the absorption tube or the conical flasks with a stream of  $\text{CO}_2$  or other inert gas. With a volumetric pipet, add an excess of standard 0.025 N iodine solution to the  $\text{Zn}(\text{C}_2\text{H}_3\text{O}_2)_2$  absorbant, remembering that 1.00 ml. iodine reacts with 0.400 mg. sulfide. Introduce 5 ml. concentrated HCl, stopper, and shake. In case 2 flasks are used, apply nearly all of the iodine to the first flask, and half of the acid to each flask. Immediately titrate with standard 0.025 N  $\text{Na}_2\text{S}_2\text{O}_3$ . Add 1 to 2 ml. starch indicator when the color turns pale straw, and complete the titration to the first disappearance of the blue color. Determine the blank titration by taking all of the reagents through the entire procedure. For best results, check the over-all technique by carrying a known ZnS standard suspension through the entire evolution process, and compare the sulfide recovery against a direct titration of an identical volume of ZnS standard suspension.

$$\text{Total sulfide, milligrams per liter} = \frac{[(A \times B) - (C \times D)] \times 16000}{\text{milliliters of sample}}$$

where  $A$  = milliliters of standard iodine solution used,

$B$  = normality of standard iodine solution,

$C$  = milliliters of standard  $\text{Na}_2\text{S}_2\text{O}_3$  titration, and

$D$  = normality of standard  $\text{Na}_2\text{S}_2\text{O}_3$  titrant.

If the sample has been collected in the field and preserved with  $\text{Zn}(\text{C}_2\text{H}_3\text{O}_2)_2$  and  $\text{NaOH}$  shake the bottle to suspend the  $\text{ZnS}$  precipitate uniformly and rapidly withdraw a measured portion of the suspension. With a volumetric pipet add an excess of standard 0.025  $\text{N}$  iodine solution and 5 ml concentrated  $\text{HCl}$  and titrate with standard 0.025  $\text{N}$   $\text{Na}_2\text{S}_2\text{O}_3$  as described above.

**Dissolved Sulfide**—Add well below the water surface 2 ml coagulant solution and 2 ml 6  $\text{N}$   $\text{NaOH}$  to the specially collected 1 liter sample. Immediately replace the stopper in a manner to avoid entrainment and invert the bottle 15 to 20 times to create a good floc. After the floc has settled and the supernatant becomes reasonably clear (within 15 min) carefully siphon into the 1 liter aeration cylinder or wide mouthed bottle taking precautions against sulfide loss through volatilization and oxidation. Complete the determination as described under Total Sulfide above.

TABLE 48.9 CONVERSION FACTORS FOR  $\text{H}_2\text{S}$  CONCENTRATION

<i>pH</i>	<i>Factor</i>	<i>pH</i>	<i>Factor</i>	<i>pH</i>	<i>Factor</i>
5.0	0.98	6.8	0.44	7.7	0.091
5.4	0.95	6.9	0.39	7.8	0.073
5.8	0.89	7.0	0.33	7.9	0.059
6.0	0.83	7.1	0.29	8.0	0.048
6.2	0.76	7.2	0.24	8.2	0.031
6.4	0.67	7.3	0.23	8.4	0.020
6.5	0.61	7.4	0.17	8.8	0.0079
6.6	0.56	7.5	0.14	9.2	0.0037
6.7	0.50	7.6	0.11	9.6	0.0013

**Un-ionized Hydrogen Sulfide**—Determine the  $\text{pH}$  and dissolved sulfide of the original sample. Multiply the dissolved sulfide concentration by the applicable factor in Table 48.9<sup>56</sup> to obtain the un-ionized  $\text{H}_2\text{S}$  concentration. The factors are valid for a temperature of 25°C and a dissolved mineral content below 2000 mg per liter. The factors can be used in the 20° to 30°C range without significant error.

### COLORIMETRIC METHOD<sup>11.5</sup>

Some strong reductants inhibit color development. Cyanide in excess of 500 mg per liter also retards color formation. Nitrite as low as 0.5 mg per liter imparts a pale yellow color. Dye intermediates, iron cyanides, and iodide interfere in concentrations exceeding 10 mg per liter. Polysulfides, hyposulfites, and  $\text{Na}_2\text{S}_2\text{O}_3$  interfere by decomposing to sulfide in acid solution. Interference from sulfite and thiosulfate at levels of 10 to 40 mg per liter can be overcome by increasing the volume of  $\text{FeCl}_3$  solution to 6 drops and the reaction time to 5 min before the addition of  $(\text{NH}_4)_2\text{HPO}_4$ .

**Reagents** Boiled Distilled Water—This should be used for the preparation of all solutions and dilutions.

**Standard Sulfide Suspension**—Bubble  $\text{H}_2\text{S}$  for 2 min in 1 liter water containing 3 drops 1  $\text{M}$   $\text{Zn}(\text{C}_2\text{H}_3\text{O}_2)_2$  solution. Remove the excess  $\text{H}_2\text{S}$  by bringing the solu-

<sup>56</sup> Reproduced with permission from Standard Methods for the Examination of Water and Wastewater 11th Ed. The American Public Health Assn. Inc. New York 1960.

<sup>57</sup> Pomeroy R. D. Sewage Works J. 8, 572 1935 13, 496 1941 Anal. Chem. 26 571 1954

tion to a boil, and boiling for 2 to 5 min. After cooling to room temperature, transfer exactly 200 ml. well mixed suspension to a flask, add an excess (10 ml. will suffice) of standard 0.025 *N* iodine solution to react with the sulfide. Add 5 ml. concentrated HCl, stopper, shake, and immediately titrate with standard 0.025 *N* Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> to the first disappearance of the blue starch indicator color. Determine the blank titration on 200 ml. water and the reagents.

$$S, \text{ milligrams per liter} = \frac{[(A \times B) - (C \times D)] \times 16000}{E}$$

where *A* = milliliters of standard iodine solution used,

*B* = normality of standard iodine solution,

*C* = milliliters of standard Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> titration,

*D* = normality of standard Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> titrant, and

*E* = milliliters of ZnS suspension taken for titration.

Use the ZnS suspension only on the day of preparation. This standard suspension contains approximately 5 mg. per liter of S, or 0.005 mg. S per 1.0 ml.

***p*-Aminodimethylaniline Sulfate Reagent.**—(a) Cautiously add 50 ml. concentrated H<sub>2</sub>SO<sub>4</sub> to 30 ml. water, and cool to room temperature. Dissolve in this solution 27.2 g. *p*-aminodimethylaniline sulfate, and dilute to 100 ml. The discoloration occurring on standing seldom impairs the utility of the stock solution. Dispense reagents (a), (b), and (c) with a safety pipet. (b) Dilute 25 ml. stock solution with 975 ml. 1 + 1 H<sub>2</sub>SO<sub>4</sub> for use in determinations of S concentrations in the 0.2 to 20 mg. per liter range. (c) Dilute 10 ml. stock solution with 990 ml. 1 + 1 H<sub>2</sub>SO<sub>4</sub> for use in determinations of S concentrations below 5 mg. per liter.

**Ferric Chloride Solution.**—One hundred g. FeCl<sub>3</sub>·6H<sub>2</sub>O per 100 ml.

**Diammonium Hydrogen Phosphate Solution,** 40 g. per 100 ml.

**Methylene Blue Color Solution.**—(a) Dissolve 1.0 g. methylene blue dye (U.S.P. grade or Biological Stain Commission certified grade are recommended) in distilled water and dilute to 1 liter. Adjust this solution so that 1 drop (0.05 ml.) is equivalent to 1.0 mg. per liter of S. Check the methylene blue color solution by matching against the blue color developed with known sulfide standards in the colorimetric procedure. Store the color solution in a tightly stoppered bottle in the dark to maintain stability for a year. (b) Dilute 10.0 ml. stock solution to 100 ml. with distilled water to prepare a color solution equivalent to 0.1 mg. per liter of S per drop (0.05 ml.).

**Sulfuric Acid,** 1 + 1.

**Procedure. Total Sulfide.**—Collect the sample and precipitate the ZnS as described in "Samples Containing Dissolved Gases," above, under "Collection of Samples," p. 2394. Decant or siphon off 80 to 95% of the supernatant, guarding against the loss of any settled floc. Transfer the ZnS slurry to a graduated cylinder. In the presence of low-level S, measure the slurry volume, adjust if necessary with a small volume of distilled water, mix the slurry thoroughly, and withdraw by pipet two 7.5-ml. portions for color development. If the S content is relatively high, add distilled water to bring the volume to 50 or 100 ml. or other convenient total, suspend the slurry uniformly, and withdraw two 7.5-ml. portions by pipet for analysis.

Place the two 7.5-ml. samples into separate test tubes. To the first tube add 0.5 ml. *p*-aminodimethylaniline sulfate reagent (b) or (c), depending on the sulfide concentration. To the second tube add 0.5 ml. 1 + 1 H<sub>2</sub>SO<sub>4</sub>. Into each tube introduce 2 drops (0.1 ml.) FeCl<sub>3</sub> solution, stopper, and mix by several inversions.

When reagent (b) is used add 16 ml  $(\text{NH}_4)_2\text{HPO}_4$  solution to each tube 1 min after the appearance of the blue color. Wait 5 min before adding the  $(\text{NH}_4)_2\text{HPO}_4$  solution when reagent (c) is used. Mix again by inversion. Add dropwise methylene blue color solution (a) or (b) to the second tube until the color intensity in the standard matches that developed in the first tube. View vertically the blue color produced by sulfide concentrations below 3 mg per liter and horizontally in the 3 to 20 mg per liter range.

$$\text{Total sulfide milligrams per liter} = \frac{D \times F \times F}{G}$$

where  $D$  = number of drops of methylene blue color solution (a) or (b) added to second tube

$E$  = sulfide equivalent of methylene blue color solution (a) or (b) used

$F$  = milliliters of ZnS slurry remaining after decantation

$G$  = milliliters of original sample collected

If desired measure the developed color photometrically at 670  $m\mu$  against the reagent blank reference. Read the absorbance of very dark solutions at 720  $m\mu$ . Prepare the calibration curve from dilutions of standardized ZnS suspensions carried through the entire procedure.

**Dissolved Sulfide**—Clarify the sample with 2 ml coagulant solution and 2 ml 6  $N$  NaOH as described in the procedure for dissolved sulfide in Iodometric Method under Sulfide p 2486 above. Complete the determination colorimetrically on a suitable aliquot of the supernatant.

**Un-ionized Hydrogen Sulfide** See the procedure for un-ionized hydrogen sulfide in Iodometric Method under Sulfide above.

### SULFITE <sup>11</sup>

This method is designed primarily for the routine control of boiler feedwaters subject to sulfite treatment. Reductants like sulfide and certain heavy metal ions react similarly to sulfite. Copper catalyzes the oxidation of sulfite on exposure to air especially at warm temperatures.

**Reagents** Standard Potassium Iodate Titrant—Dissolve 0.566 g  $\text{KIO}_3$  dried at 120°C and 0.5 g  $\text{NaHCO}_3$  in distilled water and dilute to 1000 ml. The equivalence of this titrant is 1.0 mg  $\text{Na}_2\text{SO}_3$  per 1.00 ml.

Potassium Iodide Solution 50 g per liter

Starch Indicator

Hydrochloric Acid 1 + 1

**Procedure**—Place 10 ml 1 + 1 HCl in a 250 ml flask. Rapidly add 100 ml sample submerging the pipet tip below the acid surface to minimize air exposure. After adding 1 ml starch indicator solution and 5 ml KI solution titrate with standard  $\text{KIO}_3$  titrant to the first appearance of a persistent blue color. Determine the blank titration by carrying 100 ml distilled water through the complete procedure.

$$\text{SO}_3 \text{ milligrams per liter} = (A - B) \times 6.35$$

$$\text{Na}_2\text{SO}_3 \text{ milligrams per liter} = (A - B) \times 10$$

where  $A$  = milliliters of titration for sample

$B$  = milliliters of titration for blank

ANIONIC SURFACTANTS (SYNTHETIC DETERGENTS) <sup>2</sup>

Despite the common positive interferences, the methylene blue colorimetric method often suffices for most control operations. The carbon adsorption method, on the other hand, is specific and accurate for low alkyl benzene sulfonate (ABS) concentrations in water. The length and complexity of the carbon adsorption method, however, restrict its application to those situations in which a differentiation between true ABS and interferences is required. In such an event, the analysis can be completed by infrared measurements or by a methylene blue colorimetric finish.

All glassware must be thoroughly cleansed with 1 + 1 HCl and rinsed with distilled water to guard against high values resulting from adsorbed ABS contamination.

## METHYLENE BLUE COLORIMETRIC METHOD

Organic sulfates, sulfonates, carboxylates, phosphates, and phenols interfere positively by complexing methylene blue. Inorganic cyanate, thiocyanate, chloride, and nitrate also contribute a positive interference by forming ion pairs with methylene blue. Organic materials, especially amines, which compete with the methylene blue in the reaction, can cause low results. Positive errors are more commonplace, however, in the determination of anionic surfactants in water.

**Reagents.** Standard Alkyl Benzene Sulfonate Solution.—(a) Dissolve 1.000 g. alkyl benzene sulfonate in distilled water, and dilute to 1000 ml. A pure grade of ABS can be obtained from the Association of American Soap & Glycerine Producers, 295 Madison Ave., New York 17, N. Y.) (b) Dilute 10.00 ml. stock solution to 1000 ml. with distilled water to form a standard solution containing 0.010 mg. ABS per 1.00 ml.

**Methylene Blue Reagent.**—(a) Dissolve 0.1 g. methylene blue in 100 ml. distilled water. (b) Transfer 30 ml. solution (a) to a 1-liter mixing cylinder; add 500 ml. distilled water, 6.8 ml. concentrated  $\text{H}_2\text{SO}_4$ , and 50 g.  $\text{NaH}_2\text{PO}_4 \cdot \text{H}_2\text{O}$ ; shake until the salt dissolves, and dilute to the mark with distilled water to form the reagent.

**Wash Solution.**—Carefully add 6.8 ml. concentrated  $\text{H}_2\text{SO}_4$  to 500 ml. distilled water in a 1-liter mixing cylinder, add 50 g.  $\text{NaH}_2\text{PO}_4 \cdot \text{H}_2\text{O}$ , shake until the salt dissolves, and dilute to the mark with distilled water.

Sodium Hydroxide, 1 N.

Sulfuric Acid, 1 N.

Phenolphthalein Indicator.

Chloroform.

**Procedure.**—Select a sample volume containing 0.04 to 0.2 mg. ABS, and, if necessary, dilute to 100 ml. with distilled water. For small amounts of ABS, take the following sample volumes: 400 and 250 ml., when the ABS concentration falls in the 0.025 to 0.08 mg. per liter and 0.08 to 0.40 mg. per liter ranges respectively.

Prepare the following ABS standards in 100 ml. volume with distilled water: 0, 0.010, 0.030, 0.050, 0.070, 0.090, 0.110, 0.130, 0.150, and 0.200 mg. Treat the blank and standards exactly as the sample throughout the entire procedure.

Make the sample alkaline to phenolphthalein indicator with 1 N NaOH, acidify with 1 N  $\text{H}_2\text{SO}_4$ , and transfer to a separatory funnel. Add 10 ml.  $\text{CHCl}_3$  and 25 ml. methylene blue solution, rock vigorously for 30 min., and wait for the phases to separate. Avoid excessive agitation in order to minimize emulsion difficulties. Break up any emulsion by gentle stirring with the flattened end of a glass rod.

Drain the clear  $\text{CHCl}_3$  layer into a second separatory funnel and rinse the delivery tube of the first separatory funnel with 2 ml  $\text{CHCl}_3$ . Repeat the extraction process 3 times with 10 ml  $\text{CHCl}_3$  on each occasion. If the blue color in the aqueous phase becomes faint or disappears replenish with an additional 20 ml methylene blue reagent. Add 50 ml wash solution to the combined  $\text{CHCl}_3$  extracts in the second separatory funnel and shake vigorously for 30 sec. Filter the organic layer through a glass wool or cotton plug into a 100 ml volumetric flask. Repeat the washing operation 2 more times with 10 ml portions  $\text{CHCl}_3$ . Rinse the filter and glass wool or cotton plug with  $\text{CHCl}_3$  and add the washing to the volumetric flask. Make up the collected extracts and washings to the mark with  $\text{CHCl}_3$  mix and measure the absorbance at 652  $m\mu$  against a reference of pure  $\text{CHCl}_3$ .

$$\text{ABS milligrams per liter} = \frac{\text{milligrams of ABS} \times 1000}{\text{milliliters of sample}}$$

### CARBON ADSORPTION METHOD<sup>58</sup>

**Reagents** Benzene Alcohol Solution—Mix 500 ml benzene (thiophene free) 420 ml methyl alcohol and 80 ml 0.5 N KOH

**Buffer Solution**—Dissolve 6.8 g  $\text{KH}_2\text{PO}_4$  in 1 liter distilled water and adjust to pH 6.8 to 6.9 with 6 N NaOH

**ABS Extracting Solution**—Four hundred mg (20 drops) 1-methylheptylamine + 400 ml  $\text{CHCl}_3$ . Prepare daily

Hydrochloric Acid Concentrated

Sulfuric Acid 1 N

Sodium Hydroxide 1 N

1-Methylheptylamine

Petroleum Ether (b.p. 35 to 60 C.)

Methyl Alcohol Absolute

Ethyl Alcohol 95%

Chloroform

Carbon Disulfide

Carbon Tetrachloride

**Procedure** Purification of Activated Carbon—Remove the impurities in each 100 g unground 30 mesh activated carbon (Nuchar C 190 a product of West Virginia Pulp & Paper Co. 230 Park Ave. New York 17 N. Y. has proved satisfactory) by boiling 1 hr. with 1 liter benzene alcohol solution filtering the carbon and washing with 100 ml methyl alcohol. Save the filtrate and washings and evaporate to dryness on a steam bath. (An acceptable carbon should produce a soluble organic residue less than 10 mg exclusive of any residue from the solvent.)

**Adsorption of ABS on Carbon**—Select a sample volume containing 10 to 20 mg ABS. If 2 l or less are required shake the sample vigorously for 2 min with 10 g granular activated carbon in a 2 l glass stoppered mixing cylinder. Filter off the carbon on a medium porosity sintered glass Buchner funnel. Pass samples in excess of 2 l through a carbon column at the rate of 10 g p.h. or less. For this purpose charge a glass column 5 cm in dia. and 600 cm long with a total of 100 g unground 30 mesh activated carbon distributed as illustrated in Fig. 48.9<sup>59</sup>. Use

<sup>58</sup> Salice E. M. *et al.* Anal. Chem. 28, 1822 (1956)

<sup>59</sup> Reproduced with permission from Standard Methods for the Examination of Water and Wastewater 11th Ed. The American Public Health Assn. Inc. New York 1960



stainless steel or brass wire screens, *B*, to divide the carbon into sections of 20, 30, 40, and 10 g.

Prepare the following ABS standards in 18 l. distilled water: 25, 20, 15, 10, 5, and 0 mg. ABS. Mix thoroughly in a 5-gal. glass container, and by means of a synthetic rubber-like tubing, siphon each standard through the carbon column. Treat the blank and standards exactly as the sample throughout the entire procedure.

**Solvent Extraction of ABS.**—Transfer the carbon from the Büchner funnel to a porcelain evaporating dish. Handle each of the 4 carbon sections from the glass column independently. Transfer each carbon section to a separate dish. After the carbon has been dried at 105° to 110°C., brush into separate 2-l. bottles or flasks having standard taper necks, add 1 liter benzene-alcohol solution and boiling chips, and reflux under an air condenser for 1 hr. Filter to dryness under suction through a Büchner funnel, then arrest the suction, and mix the carbon with 100 ml. methyl alcohol, using a glass rod. Remove the wash under suction. Wash with a second 100-ml. portion methyl alcohol. Return the carbon to the flask, add 1 liter benzene-alcohol solution, and again reflux for 1 hr. Repeat the filtration and washing with methyl alcohol. Reject the carbon. Combine the filtrates and washings in a large (3-l.) beaker, and evaporate the solvent over a steam bath. Accelerate the evaporation here and hereafter by directing a stream of air or nitrogen onto the surface. When the extracts from the 20-, 30-, and 40-g. carbon sections get down to a manageable volume, combine in a single beaker. Continue to handle the extract from the 10-g. section independently, however. Upon evaporation of the solvent, dissolve the residue in 50 ml. distilled water, and transfer to a 250-ml. standard taper flask. Rinse the beaker with 30 ml. concentrated HCl, and add slowly to the flask to control the CO<sub>2</sub> evolution. Wash the beaker with 50 ml. distilled water, add the washing to the flask, and reflux for 1 hr. under an air condenser. After removing the condenser, boil down to a volume of 20 to 30 ml., then take down to near dryness on a steam bath. Dissolve the residue in 100 ml. distilled water, neutralize with 1 *N* NaOH to pH 8 to 9, and extract with 50 ml. petroleum ether. If necessary, introduce up to 70% ethyl alcohol to break any emulsion. Wash the petroleum ether with two 25-ml. portions distilled water, reject the organic layer, and add the washings to the aqueous layer. Boil off any alcohol that may have been applied. Make the cooled solution just acidic to litmus with 1 *N* H<sub>2</sub>SO<sub>4</sub>, transfer to a 250-ml. separatory funnel, add 50 ml. buffer solution and 2 drops (0.10 ml.) 1-methylheptylamine, and shake vigorously. Introduce 50 ml. ABS extracting solution and 25 ml. CHCl<sub>3</sub>, shake for 3 min., drain the lower organic layer, and filter through a glass-wool plug wet with CHCl<sub>3</sub>. Rinse the glass-wool plug with 10 ml. CHCl<sub>3</sub> and add to the extract. If necessary, conduct the filtration under suction.<sup>60</sup> Repeat the extraction with 50 ml. ABS extract-

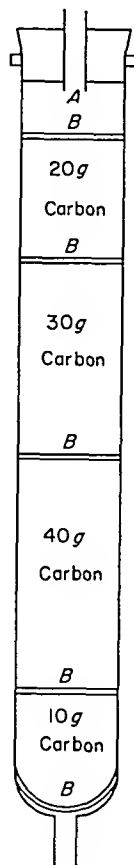


FIG. 48-9. Carbon Adsorption Tube: *A*, Glass Tube; *B*, Wire Screen.

<sup>60</sup> Fairing, J. D., and Short, F. R., *Anal. Chem.*, **28**, 1827, 1956.

ing solution and 25 ml  $\text{CHCl}_3$  shaking for 2 min. Perform a third extraction with 5 ml ABS extracting solution and 45 ml  $\text{CHCl}_3$ . Combine the extracts in a 400 ml beaker and evaporate over a steam bath. Transfer the residue with 10 ml  $\text{CHCl}_3$  to a 50 ml beaker together with three 5 ml rinses of  $\text{CHCl}_3$ . Evaporate to dryness and for 30 min longer over a steam bath to remove the excess amine. Complete the procedure by the methylene blue colorimetric method or infrared measurement.

**Methylene Blue Colorimetric Method Finish**—Take up the residue in a suitable volume of distilled water, develop the color, and measure the absorbance at  $659 \text{ m}\mu$  as already described.

**Infrared Measurement Finish**—Dissolve the residue in 1 ml  $\text{CS}_2$  or  $\text{CCl}_4$  and filter through a glass wool plug placed in a funnel stem of 2 mm bore. Collect the filtrate in a 2 or 5 ml volumetric flask and dilute to the mark by passing several rinses of the beaker through the filter. Run the infrared absorption curve on a portion of the well mixed sample from 9.0 to  $10.5 \mu$  against a solvent blank. Measure the absorbance of the 9.6 and  $9.9 \mu$  peaks using base lines from 9.5 to  $9.8 \mu$  and from 9.8 to  $10.1 \mu$ . From the appropriate calibration curves report the ABS values based on each wavelength separately. For positive qualitative identification of ABS, evaporate 0.5 to 1.0 ml portion of the well mixed sample on a NaCl flat and record the absorption spectrum in the  $2\text{--}15 \mu$  range.

$$\text{ABS milligrams per liter} = \frac{\text{milligrams of ABS} \times 1000}{\text{milliliters of sample}}$$

### TANNIN AND LIGNIN <sup>61</sup>

Other reducing materials react like tannin and lignin. Unless either tannin or lignin is definitely known to be present in the water under examination, the results of this determination may logically be reported in the more general terms of tannin like, lignin like, or simply hydroxylated aromatic compounds.

**Reagents** **Standard Solution**—(a) Weigh 1.000 g of the tannic acid, tannin, or lignin compound that is being used for boiler water treatment or is known to be a contaminant of the water sample. Dissolve in distilled water and dilute to 1000 ml. (b) Dilute 50.00 ml stock solution to 1000 ml with distilled water to form a standard solution containing 0.050 mg active ingredient per 100 ml. (c) Dilute 10.00 ml stock solution to 1000 ml with distilled water to form a standard solution containing 0.010 mg active ingredient per 100 ml.

**Tannin Lignin Reagent**—Dissolve 100 g  $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$ , 20 g phosphomolybdic acid, and 50 ml 85%  $\text{H}_3\text{PO}_4$  in 750 ml distilled water. Reflux the solution for 2 hr, cool, and dilute to 1 liter with distilled water.

**Saturated Sodium Carbonate Solution**—Dissolve 200 g  $\text{Na}_2\text{CO}_3$  in 500 ml warm distilled water and dilute to 1 liter. Store in a rubber stoppered bottle.

**Procedure**—If necessary, clarify the sample by centrifuging or filtration. Pipet into a 100 ml Nessler tube a sample volume containing 0.02 to 0.15 mg tannic acid or 0.05 to 0.40 mg lignin, or any other appropriate concentration of the particular compound that is being applied for boiler water treatment or is known to be a contaminant of the water sample. If necessary, dilute to 50.0 ml with distilled water.

Prepare the following tannic acid standards: 0.0010, 0.0030, 0.0050, 0.0100, and

<sup>61</sup> Berk, A. A., and Schroeder, W. C., *Ind. Eng. Chem. Anal. Ed.* 14, 456 (1942).

0.150 mg.; or a lignin standard series of 0, 0.050, 0.100, 0.200, 0.300, and 0.400 mg. Dilute the standards to 50 ml. in 100-ml., tall-form Nessler tubes.

Treat the blank and standards exactly as the sample throughout the entire procedure. Add 2 ml. tannin-lignin reagent, mix, and after 5 min., introduce 10 ml. saturated  $\text{Na}_2\text{CO}_3$  solution. Mix well and allow the color to develop for 10 min. Measure the absorbance at 700  $\text{m}\mu$  in a spectrophotometer or at 600 to 700  $\text{m}\mu$  in a filter photometer, using a 5-cm. cell and a reagent blank as the reference. Alternatively, match the colors of the sample and standards visually.

## TASTE AND ODOR <sup>2</sup>

Taste and odor determinations are made on waters destined for human consumption or for the processing of food products. Odor tests are additionally performed on polluted and waste waters for the purpose of detecting domestic and industrial discharges.

The elevated temperature of 60°C. has been found to improve the sensitivity of the odor test on some samples. The taste test is conducted at 40°C. because the temperature approximates that of the human body, thereby creating no sensation of hot and cold.

The threshold odor number is defined as the number of times the water sample must be diluted to yield a barely detectable odor. Cold and hot threshold tests are carried out at 40° and 60°C. respectively.

A number of measures will contribute to the success of taste and odor observations. The room reserved for the tests should be relatively still and free of odors from tobacco smoke, food, scented soaps, shaving lotions, perfumes, or volatile agents (chemicals) of any description. Participants should refrain from smoking or eating immediately before the test. Where possible, the tests should be conducted on a blind basis whereby one person prepares and codes the sample dilutions for a panel of observers. A series of dilutions should be presented to the participants in a sequence proceeding from the most dilute to the most concentrated. Frequent 15- to 30-min. rest intervals should punctuate the observation periods in order to minimize fatigue of the taste and odor senses.

**Odor-Free Water.**—Pass tap water through the odor-free water generator (Fig. 48-10) at a rate of 1 liter per minute. Discard the initial output of the generator, as it may contain fine carbon particles. Carefully eliminate any residual chlorine in the effluent with an equivalent amount of 0.01  $N$   $\text{Na}_2\text{SO}_3$  or  $\text{Na}_2\text{S}_2\text{O}_3$ .

**Procedure.**—Clean all glassware internally and externally with an unscented cleanser or acid cleaning solution, and finally rinse several times with odor-free water just before use.

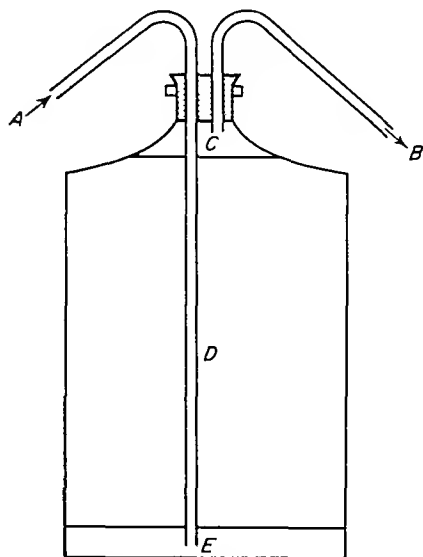


FIG. 48-10. Generator of Odor-Free Water: A, Direction of Tap Water Flow; B, Direction of Odor-Free Water Flow; C, Layer of Glass Wool; D, 1-gal. Jug or Bottle Containing Granular, 4 by 10 Mesh, Activated Carbon; E, 1-in. Layer of Pea-Size Gravel.

**Odor Quality**—Transfer 200 ml sample or an aliquot diluted to 200 ml with odor free water to a 500 ml glass stoppered wide mouthed flask. Prepare a 200 ml odor free water blank in another flask. Place both flasks in a water bath or on a hot plate adjusted at 40°C or 60°C. When the blank and sample reach the proper temperature (within 1°C) shake the flasks remove the stoppers and observe the odor of the blank first and then the sample. Use the qualitative descriptions in Table 48-10<sup>69</sup> as a guide in identifying the odor.

TABLE 48-10 QUALITATIVE DESCRIPTION OF ODORS

Nature of Odor	Common Resemblance or Contributory Factor	Causative Microorganisms
<i>Aromatic (spice)</i>	Camphor cloves lavender, lemon	<i>Synura</i>  <i>Asterionella</i> <i>Aphanizomenon</i> <i>Coelosphaerium</i> <i>Mallomonas</i>
Cucumber		
<i>Balsamic (flowers)</i>	Geranium violet vanilla	
Geranium		
Nasturtium		
Sweetish		<i>Uroglenopsis</i> <i>Dinobryon</i> <i>Anabaena</i>
Violet		
<i>Chemical</i>	Industrial wastes or treatment chemicals	
Chlorinous	Free chlorine	
Hydrocarbon	Oil refinery wastes	
Medicinal	Phenol and iodoform	
Sulfuretted	Hydrogen sulfide	
<i>Disagreeable</i>	Very unpleasant	
Fishy		
Pippen		
Septic	Stale sewage	
<i>Earthy</i>	Damp earth	
Peaty	Peat	
<i>Grassy</i>	Crushed grass	
<i>Musty</i>	Decomposing straw	
Moldy	Damp cellar	
<i>Vegetable</i>	Root vegetables	

**Taste Quality**—Taste only a safe water by holding 10 to 15 ml of the 40 C sample in the mouth and expel after several seconds. Record the aftertaste as well as the actual taste.

**Threshold Odor Evaluation**—Prepare a series of 500 ml glass stoppered wide-mouthed flasks containing 200 50 12 and 2 8 ml of the water sample. Dilute all the samples except the first to 200 ml with odor free water. Set up a reference blank consisting of 200 ml odor free water. Heat the samples and blank to 40

<sup>69</sup> Reproduced with permission from Standard Methods for the Examination of Water and Wastewater 11th Ed. The American Public Health Assn. Inc. New York 1960.

or 60°C. Shake the reference flask first, remove the stopper, and sniff. Repeat the operation with the other flasks, proceeding progressively from the most dilute to the final undiluted sample. Note the flask in which the odor is first observed, and then prepare a second, more refined series of dilutions indicated in Table 48-11.<sup>62</sup>

TABLE 48-11. DILUTIONS FOR VARIOUS ODOR INTENSITIES

*Sample Volume (ml.) in Which Odor is First Noted*

200	50	14	2.8
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*Volume (ml.) of Sample to be Diluted to 200 ml.*

200	50	14	5.0
130	40	11	3.3
100	29	9.1	2.2
67	20	6.7	1.3
50	14	5.0	1.0

Record the dilution in which the odor is first detected in the new series, and calculate the threshold odor number for the stated temperature thus:

$$\text{Threshold odor number} = \frac{A + B}{A}$$

where  $A$  = sample volume,

$B$  = volume of odor-free water.

### TURBIDITY<sup>2, 11</sup>

Turbidity depends on the amount and particle size of the suspended matter in water. The determination is performed for the purpose of ascertaining the clarity of drinking and process waters. The standard instrument for measuring turbidity in the range 25 to 1000 units is the Jackson candle turbidimeter (Fig. 48-11). The instrument consists of an arbitrarily calibrated glass tube (see Table 48-12<sup>62</sup>) enclosed in a metal tube, which is supported over a candle.

The turbidity results obtained with photoelectric instruments may differ from the values secured with the Jackson candle turbidimeter, even when the instruments are calibrated against properly standardized suspensions.

Turbidity in the range 5 to 100 units is often determined in routine control by recourse to bottle standards.

**Stock Suspension.**—The best suspensions are prepared with natural turbid water from the same source as the test water. Suspended matter or bottom sediments from the body of water supplying the test samples represent good alternatives.

The objective is to suspend the material causing the turbidity in the given water supply, when such known treatment chemicals as alum or carbon are involved and are responsible.

Where the results with any of these materials prove unsatisfactory, Fuller's earth or wet-ground diatomaceous earth are often relied upon for the production of the stock suspension. Approximately 5 g. dry material are thoroughly mixed with 1 liter distilled water, and allowed to stand for 24 hr. The supernatant is withdrawn for subsequent dilutions without disturbing the sediment, and the turbidity is standardized with the Jackson candle turbidimeter.

TABLE 48-12. GRADUATION OF JACKSON CANDLE TURBIDIMETER

Depth of Suspension, <sup>a</sup> Centimeters	Turbidity Units	Depth of Suspension, <sup>a</sup> Centimeters	Turbidity Units	Depth of Suspension, <sup>a</sup> Centimeters	Turbidity Units
2.3	1000	7.3	300	19.6	110
2.6	900	7.5	290	21.5	100
2.9	800	7.8	280	22.6	95
3.2	700	8.1	270	23.8	90
3.5	650	8.4	260	25.1	85
3.8	600	8.7	250	26.5	80
4.1	550	9.1	240	28.1	75
4.5	500	9.5	230	29.8	70
4.9	450	9.9	220	31.8	65
5.5	400	10.3	210	34.1	60
5.6	390	10.8	200	36.7	55
5.8	380	11.4	190	39.8	50
5.9	370	12.0	180	43.5	45
6.1	360	12.7	170	48.1	40
6.3	350	13.5	160	54.0	35
6.4	340	14.4	150	61.8	30
6.6	330	15.4	140	72.9	25
6.8	320	16.6	130		
7.0	310	18.0	120		

<sup>a</sup> Measured from inside bottom of glass tube.

governing volumes, pH, and extraction times must be exactly reproduced in blank, standards, and sample. The sensitivity of the method requires the thorough cleansing of all glassware with dilute  $\text{HNO}_3$ , followed by rinses with Zn-free water and dithizone solution. A wise precaution against contamination is the segregation of the glassware used for the Zn determination. As in the case of all dithizone methods, the photosensitivity of dithizone and dithizonates imposes the necessity for promptly performing the extractions out of the range of strong light. Chloroform,  $\text{CCl}_4$ , and reagents of a grade satisfactory for dithizone work should be used exclusively.

**Reagents.** Deionized Distilled Water or Redistilled Water.—These should be used for the preparation of all solutions and dilutions.

**Standard Zinc Solution.**—(a) Dissolve 0.1000 g. pure Zn metal (30-mesh) in a slight excess (about 1 ml.) of 1 + 1 HCl, and dilute to 1000 ml. (b) Dilute 10.00 ml. stock solution to 100 ml. to form a standard solution containing 0.010 mg. per 1.00 ml. Prepare daily.

**Dithizone Solution.**—Dissolve 50 mg. diphenylthiocarbazone (dithizone) in 1 liter  $\text{CCl}_4$ . Stopper tightly and store in the refrigerator. If necessary, purify the dithizone as described in "Dithizone-Carbon Tetrachloride Solution," under "Cadmium," p. 2408, above.

**Sodium Acetate Solution, 0.5 M, 68 g.  $\text{NaC}_2\text{H}_3\text{O}_2 \cdot 3\text{H}_2\text{O}$  per liter.**—Free the solution of heavy metal impurities by shaking with repeated 10-ml. portions dithizone

solution until the final dithizone portion remains an unchanging green color. Then shake the solution with pure  $\text{CHCl}_3$  or  $\text{CCl}_4$  to remove the excess dithizone.

**Sodium Thiosulfate Solution** 50 g  $\text{Na}_2\text{S O}_3 \cdot 5\text{H}_2\text{O}$  in 100 ml Water—Free the solution of heavy metal impurities by dithizone extraction as described for 0.5 M sodium acetate solution in the preceding paragraph.

**Thiosulfate Acetate Wash Solution**—Mix 225 ml 0.5 M  $\text{NaC}_2\text{H}_3\text{O}_2$  solution, 10 ml  $\text{Na}_2\text{S O}_3$  solution and 40 ml 1 + 9  $\text{HNO}_3$ . Dilute to 500 ml with water.

**Sodium Sulfide Solution** 1 g  $\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$  per 100 ml—Immediately before use dilute 40 ml of this solution to 1 liter with water.

**Bromocresol Green Indicator Solution** 0.1 g per 100 ml

**Hydrochloric Acid Concentrated**

**Hydrochloric Acid 0.1 N**

**Carbon Tetrachloride**

**Sodium Sulfate**

**Procedure**—If necessary first remove interfering amounts of organic matter by the steps described in Cadmium p 2407 above.

Select a sample volume containing 0.01 to 0.04 mg Zn. In the case of a potable water that has been preserved with acid, evaporate the sample (up to 100 ml) to dryness in a silica dish and take up the residue with 20 to 100 ml 0.1 N  $\text{HCl}$ . Prepare a blank and a series of Zn standards (0.010, 0.020, 0.030 and 0.040 mg) with sufficient water and  $\text{HCl}$  to give an acidity of 0.1 N and a total volume equal to the sample. Treat the blank and standards exactly as the sample throughout the procedure. Using bromocresol green as an external or internal indicator adjust the pH to 4.6 to 5.5 with 0.5 M  $\text{NaC}_2\text{H}_3\text{O}_2$ . Add 5 ml  $\text{Na}_2\text{S O}_3$  solution and mix. Transfer to a separatory funnel, add 10 ml dithizone solution and shake vigorously for 2.0 min. Drain the organic layer into a second clean separatory funnel. Repeat the dithizone extraction 2 more times and transfer the extracts to the second separatory funnel. Reject the aqueous layer. Shake the combined extracts with two 5 ml portions thiosulfate acetate wash solution. Then wash with 5 ml water. Finally shake with three 5 ml portions  $\text{Na}_2\text{S}$  solution or until the last portion remains colorless. Filter the red zinc dithizonate layer through a small filter paper or a cotton or glass-wool plug or a fritted glass funnel containing a 1 g layer of  $\text{Na}_2\text{SO}_4$  into a 50 ml volumetric flask. Wash the filter with a little  $\text{CCl}_4$  and add the washing to the volumetric flask. Dilute to the mark with  $\text{CCl}_4$ , mix well, then determine the absorbance at 535  $\text{m}\mu$  against a reference of pure  $\text{CCl}_4$  or the reagent blank. When a  $\text{CCl}_4$  reference is used, correct the sample result by deducting the Zn content of the reagent blank carried through the entire procedure. For visual color matching, place the colored organic layer in a dry 50 ml Nessler tube and compare the samples and standards by viewing transversely against a white background.

$$\text{Zn milligrams per liter} = \frac{A \times 1000}{\text{milliliters of sample}} \times \frac{B}{C}$$

where  $A$  = milligrams of Zn found photometrically or visually. The ratio  $B/C$  applies only when a large sample is digested for removal of organic matter interference; the volume then made up to  $B$  and an aliquot  $C$  taken from it for color development.

ZINCON METHOD <sup>11, 63</sup>

The following interferences affect the zincon method: 5 mg. per liter Al or Mn; 7 mg. per liter ferric ion; 9 mg. per liter ferrous ion; 10 mg. per liter Cr; 20 mg. per liter Ni or polyphosphate; 30 mg. per liter Cu or Co; and 50 mg. per liter chromate.

**Reagents.** Deionized Distilled Water or Redistilled Water.—These should be used in the preparation of all solutions and dilutions.

**Standard Zinc Solution.**—Prepare as described in "Dithizone Method," immediately above.

**Zincon Reagent.**—Dissolve 0.130 g. 2-carboxy-2'-hydroxy-5'-sulfoformazylbenzene (zincon) in 2 ml. 1 *N* NaOH, and dilute to 100 ml. with water. Prepare this red solution weekly, and refrigerate to maintain its stability.

**Buffer Solution.**—Dilute 213 ml. 1 *N* NaOH to 600 ml. with water. Dissolve 37.3 g. KCl and 31.0 g. H<sub>3</sub>BO<sub>3</sub> in the solution, and dilute to 1 liter.

**Chloral Hydrate Solution,** 10.0 g. per 100 ml.—Dispense this reagent with a safety pipet.

**Potassium Cyanide Solution,** 1.00 g. per 100 ml.—Dispense this reagent with a safety pipet.

Sodium Hydroxide, 1 *N*.

Sodium Hydroxide, 6 *N*.

Hydrochloric Acid, Concentrated.

Sodium Ascorbate.

**Procedure.** Preliminary Sample Treatment. *Total Zinc.*—Measure 2 portions of 50.0 ml. well-mixed sample into a beaker. When the sample contains color or turbidity, use the second portion as a sample blank to which all reagents are added except chloral hydrate. Substitute distilled water for the chloral hydrate in this situation. Add 1.0 ml. concentrated HCl, heat to boiling, and boil the solution for 5 min. Cool to room temperature, then, with the aid of pH paper, adjust the solution to pH 7 by the dropwise addition of 6 *N* NaOH. Transfer to a 50-ml. volumetric flask, and dilute with distilled water to the mark.

*Dissolved Zinc.*—Decant the supernatant from a settled sample and pass through a cellulose acetate membrane filter or an ashless, fine-textured, retentive filter paper. Reject the initial 25 ml. filtrate.

**Color Development.**—Select a sample volume containing 0.0002 to 0.05 mg. Zn. Dilute or concentrate the volume to 10.0 ml., and transfer to a 100-ml. flask. Prepare in 10.0 ml. volume a blank and a series of Zn standards in the range 0.0002 to 0.050 mg. Treat the blank and standards exactly as the sample throughout the procedure. Mixing after each addition, introduce the following reagents in the order listed: 0.5 g. sodium ascorbate, if the sample contains more than 0.2 mg. per liter Mn; 1 ml. KCN solution; 5 ml. buffer solution (or enough to bring the pH to 9.0); 3 ml. zincon reagent; and 3 ml. chloral hydrate solution. Within 2 to 5 min., read the absorbance at 620 m $\mu$  against the reagent blank or the special sample blank. Use a 1-cm. cell for measurements in the 0.001 to 0.050 mg. Zn range, and a 2.3-cm. cell in the range up to 0.025 mg.

$$\text{Zn, milligrams per liter} = \frac{\text{milligrams of Zn} \times 1000}{\text{milliliters of sample}}$$

<sup>63</sup> Platte, J. A., and Marcy, V. M., *Anal. Chem.*, **31**, 1226, 1959.



## *Chapter 49*

# **WATER: BACTERIOLOGICAL EXAMINATION**

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An essential of life is a water supply of ample volume for all needs, of acceptable and pleasing quality and above all free from pollution and thus safe for human consumption. Frequently treatment processes of various types are necessary to yield such a desirable water supply. These treatment processes are designed to eliminate pollution and thus to make the treated water of safe as well as satisfactory quality. Pollution usually finds access to a source of water as a result of the unfortunate but common practice of dispensing of all of the waste products of municipal and industrial operations by discharge into the nearest body of water without consideration that the water may be required for a source of domestic supply of drinking water by a large or small downstream community. Such wastes contain bacteria of many kinds including potentially the specific organisms that are the causative agents of disease in man. Many other types of bacteria are normal habitants of soil and decaying vegetation and will enter water through the agency of surface drainage or other means. Thus bacteria can be an indication of pollution of water and their absence or removal by treatment a measure of the safety of the water and the effectiveness of treatment procedures.

Technics for the detection and quantitative measurement of bacteria in water are thus of major importance in assuring the suitability of any water supply for dietetic uses or other domestic purposes.

To fully understand the technical laboratory procedures for the bacteriological examination of water and the interpretation of the results of such examinations a knowledge is essential of the specific microorganisms that are associated with pollution, their functions, life processes and biochemical reactions, and in particular, their function in our environment.

## **BACTERIA INDICATIVE OF POLLUTION**

Although many types of bacteria may be found in water originating from the soil and air, only those which result from pollution by sewage or other wastes are important in relation to the sanitary quality and safety of water. The significant ones are, of course, the pathogenic types which come from the bodies of persons who are ill and are transmitted through the agency of the water to uninfected per-

sons. However, to detect and enumerate pathogenic bacteria in water is not practical. Pathogenic bacteria may be present in only relatively small numbers, far fewer than many other species, and the technical procedures required to isolate them are difficult and subject to gross interferences by the predominating numbers of other organisms.

It is also possible that a water supply may be heavily polluted and yet pathogenic microorganisms be absent in the test portions examined. As a result the detection of specific pathogenic bacteria in water is not at all feasible and is seldom undertaken. The important factor remains that a polluted water can be regarded as containing pathogenic species and that these are absent in an unpolluted water supply. The important problem, therefore, is the detection and enumeration of types of bacteria in water which by their presence provide a quantitative indication of pollution, especially sewage pollution.

An indicator organism for detecting pollution of water should be one which is specific, that is, it is always found in sufficient numbers in sewage and is not found anywhere else in nature, one which will survive longer under unfavorable environmental conditions than the pathogenic types potentially present in the sewage, and one which is readily detected quantitatively by simple and rapid laboratory technics. An organism, known as *Escherichia coli*, is a normal inhabitant of the intestinal tracts of warm-blooded animals, particularly human beings. It is discharged in huge numbers from the intestinal tract and thus is present in community wastes or sewage. *Esch. coli* is a parasitic bacterium, nonpathogenic, and in general will survive in water as long as the pathogenic bacteria that are discharged by persons ill with the enteric diseases (typhoid fever, dysentery). It is, however, closely related to other types of bacteria which have the same feeding habits, susceptibility to the environment, the same appearance, and the same general characteristics but which are not necessarily found only in the intestinal tracts of warm-blooded animals. These constitute a group of related bacteria.

The laboratory technics required to detect and isolate *Esch. coli* and these related bacterial forms from water are relatively simple although not as rapid as could be desired. Actually, it is necessary to consider this entire group of bacteria, and not just one individual type, as an indicator of sewage pollution. All are similar to *Esch. coli* in behavior and metabolism, but all are not normal inhabitants of the human intestinal tract. Thus, they do not all have the same significance relative to possible accompanying pathogenic bacteria. However, all are found in sewage in large numbers and thus are of equal significance as indicators of sewage pollution.

There are numerous individual bacterial types in this group, which is designated as the coliform group of bacteria. The coliform group is usually defined as a group which includes all aerobic and facultative anaerobic Gram-negative, non-sporeforming bacteria (rod shaped), capable of fermenting lactose (milk sugar) with the production of acid and gas at 35°C. in less than 48 hours.

The coliform group is divided into two main sections, the coli section, which includes *Esch. coli* and certain other individuals of similar origin, and the *Aerobacter aerogenes* section, which includes forms related to the coli section but found normally in the soil or growing vegetation. This section has as its characteristic member *Aerobacter aerogenes* which cannot be described as an intestinal type but is an organism associated with the soil and vegetation. The other members of this section are similar in their natural habitat. They may, however, gain access to the intestinal tracts of warm-blooded animals through food, and thus be intro-

duced into sewage by the same processes as the members of the coli section. Members of the aerogenes section may also be introduced into sewage through surface drainage and soil washings. The important fact is that they are present in sewage in company with the members of the coli section, although usually in smaller population densities and are indicative of sewage and sewage pollution. The coliform group as a whole therefore has been generally accepted as a significant indicator of sewage pollution when found in water. Although not an entirely satisfactory indicator it has served effectively for many years as the accepted symbol of pollution and thus of water quality.

Bacteria of the coliform group are present in sewage in huge numbers several million per milliliter. Since it is possible to detect as few as one coliform organism in 100 ml of water this group is an extremely sensitive indicator of the presence of pollution in water.

It must be understood that the coliform group is only an indicator of potential sewage or waste pollution and is not necessarily a reliable indicator of the presence of bacteria of recent fecal origin in the water being examined. Because the pathogenic bacteria are of fecal origin only it has frequently been stated that the coliform group is not a sufficiently sensitive indicator of the source or health significance of the pollution since it may at times indicate, through predominating numbers of the aerogenes section, pollution that is probably of vegetable and soil origin and is then considered to condemn water as polluted by sewage or intestinal discharges when such may not be the case.

Thus the suggestion has been urged that technics be developed which will permit detection of the bacteria of the coliform group of fecal origin only rather than of the entire group. This however does not seem altogether desirable, since the coliform group by its presence in water in appreciable densities does indicate that pollution of fecal origin or not has found access to the water supply with consequent deterioration in quality. Since the primary purpose of water treatment is to provide a water of safe and acceptable quality anything which degrades that quality should not be allowed to remain. Coliform bacteria are not normal inhabitants of water and their presence represents a condition which should not be acceptable. Differentiation of pollution into that of fecal origin and that of non fecal origin becomes of no practical significance, and the coliform group should remain the final criterion of the bacteriological quality of water.

### SAMPLING FOR BACTERIAL TESTS

As with all other analytical procedures in the examination of water an important part of the technic is the sample. Major emphasis must therefore be placed on the methods of sampling. The sample is only a very small portion of the entire volume of water under treatment and must be so collected as to represent as closely as possible the actual conditions existing in the main body of water. Thus sampling points must be selected with great care and with full consideration of these essential factors.

The essential facts relative to the significance of sampling, the location of sampling points and the storage and transportation of the samples must be understood. The samples must be representative of the water to be examined or the results will have no significance.

## SAMPLES FOR BACTERIOLOGICAL EXAMINATION

**Sample Bottles.**—Only clean, wide-mouthed, six-ounce, glass-stoppered<sup>1</sup> bottles of borosilicate or similar glass should be used for samples to be examined bacteriologically. Ordinary glass will not stand repeated heating for sterilization and may impart enough alkali to a sample to exert a bactericidal effect upon the sample. The stopper, neck, and mouth of the bottle must be protected from contamination. This is generally accomplished by covering with metal foil or heavy paper, such as milk bottle hoods, before the bottle is sterilized.

Samples for bacteriological examination must always be collected in sterilized bottles since contamination of the bottles would prevent accurate evaluation of the results. Sterilization for this purpose is accomplished by heating the bottles at 170°C. in an oven for one hour after the temperature has reached 170°C. When samples of chlorinated water are to be examined, the chlorine must be destroyed when the sample is collected. Otherwise the results will not be typical of the water at the point of collection but will represent conditions corresponding to a further contact period with the chlorine equal to the time of transportation to the laboratory. The addition of 0.1 ml. of a 10% solution of sodium thiosulfate ( $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ ) to the bottle before sterilization provides for neutralization of 15 p. p. m. chlorine for a 100-ml. sample.

**Sampling Procedures.**—Sampling stations must be selected to permit the collection of samples fully representative of the supply to be examined. Taps in distribution systems and on the discharge of pumps usually can be considered suitable. Leaking taps must be avoided since any water allowed to flow over the outer surface of the tap would contaminate the sample. Flaming of taps to insure sterility is seldom desirable. Rather the tap should be thoroughly flushed by allowing the water to flow with the valve fully opened. Restriction of the flow by partially closing the valve will be necessary to permit filling the sampling bottle without spattering.

The sterilized bottle selected for the collection of samples for bacteriological examination should be handled with care to avoid contamination. Hold the bottle at or near the bottom. Loosen the string around the protective cap and remove the stopper with the cap in place. Be sure that the exposed stopper is not contaminated by touching anything, that the lip of the bottle is not contaminated by the hands, and that the water does not flow over the hands into the bottle. Fill the bottle to within half an inch of the stopper, leaving only sufficient air space for expansion. Replace the stopper and tighten the string securely around the protective cap.

For collecting samples from wells, springs, streams, and other sources where pipe taps are not available, grasp the bottle by the bottom and plunge the open mouth down into the water, then turn the bottle while forcing it against the water or direction of flow, if any, to permit the water to flow into the open bottle without first passing over the hand.

Frequently special sampling procedures will need to be improvised for the aseptic collection of samples from some sources, particularly those which cannot be reached readily. Various types of equipment for the collection of samples below the surface of water sources are obtainable and may be employed.

**Samples for Laboratory Control of Plant Operation.**—Samples of raw water should be collected to determine the characteristics of the water that are to be

<sup>1</sup> Metal and plastic caps, nontoxic to bacteria, may be substituted.

corrected by treatment. These characteristics fluctuate in varying degrees with different water supplies and have a marked effect on plant operation. When coagulation and filtration is employed, samples of the coagulated water demonstrate the efficiency of such treatment, as do samples of filter effluent. Samples of the water as it enters the distributing system show the overall efficiency of the treatment employed. Samples from the distributing system show the character of the water delivered to the consumer and, by comparison with treated water, show the changes, if any that occur during distribution.

*Samples for Water Quality*—Generally, examination of a sample of water as it enters the distributing system and several samples from the distributing system is desirable. The number taken from the system varies with the facilities available, the size of the population served, and the purpose for which the examinations are made. Normally, samples for bacteriological examinations are collected from many scattered points on the system and samples for chemical analysis are collected from only a few points.

The quality of water supplied by wells, springs and similar sources, particularly to individual homes, often requires examination for its quality and safety for domestic uses. A series of samples from any one such source would provide the most useful information for the continuing safety of the supply. When this is impractical, a single sample may be used provided that it is collected under conditions of maximum use of the water from the source and possibly under minimum ground water sources. This may frequently indicate the poorest quality but for purposes of drinking this particular hazard should be determined. After sudden pollution or flooding of a well collection of a sample for determination of the bacterial quality is generally useless. Sampling should be postponed until the well has been thoroughly pumped out and returned to conditions bordering on normal for the particular source.

### STORAGE OF SAMPLES

The time elapsing between collection and examination should be as brief as possible and in no case should exceed 24 hours. In samples stored for more than 24 hours growth of bacteria of no sanitary significance that interfere with the laboratory tests can be anticipated. During the time elapsing between collection and examination the temperature of the sample should be maintained as closely as possible to the temperature of the source. Abrupt changes in the temperature of a sample, as for example by rapid cooling or refrigeration, may affect bacterial metabolism and result in major discrepancies in the laboratory examinations. The time and temperature of storage of all samples should be carefully recorded.

### FREQUENCY OF SAMPLING

The frequency at which samples should be collected is dependent upon the problem of quality evaluation and control and must be established for each particular instance. Sampling programs should be intelligently planned to permit full supervision of water treatment processes and evaluation of water quality. When the safety of a water depends entirely upon disinfecting treatment a constant check on the bacteriological quality of the water entering the distribution system is essential and no less than daily samples from significant points should be collected and examined.

Water from well supplies or large storage reservoirs fluctuates much less rapidly than water from small reservoirs or streams. On the other hand, water from lakes

either large or small, may fluctuate rapidly with changing winds or flow of tributary streams. Semi-annual samples from some wells may be sufficient; monthly samples may be required from others. For surface water supplies, weekly or even daily or hourly samples are necessary to control treatment processes. The frequency of plant samples depends upon the fluctuation of the raw water quality. With a fairly constant raw water, weekly samples suffice for most tests. Other supplies may require daily or even more frequent sampling. For control of chlorination a minimum of daily and more often, hourly samples may be required. For bacteriological examination, samples of raw and finished water should be examined daily where coagulation, filtration, and chlorination are practiced.

For control of the sanitary quality of water in the distributing system of public supplies, the following table may be used as a guide, although it should be understood that this is the minimum number of samples that is acceptable.

<i>Population Served</i>	<i>Minimum Number of Samples per Month</i>
2,500 and under	1
10,000	7
25,000	25
100,000	100
1,000,000	300
2,000,000	390
5,000,000	500

## RECORDS

No sample is of any value unless its identity is accurately known at the time of analysis. The few minutes spent immediately after sampling in recording the identity of the sample and other pertinent data are an essential part of the sampling technic. Such information should be complete; it should contain all of the facts that later may be needed to interpret the laboratory results properly and apply them to the control of treatment. The recording of too much data should be avoided—but not to the extent of recording too little. Prepared forms with space for basic and minimum information about the sample are a great aid. Such a form must be filled out completely and accurately for each sample collected.

Sample forms to record identifying and descriptive data for a sample should be developed to meet the requirements of specific problems of water quality control. Not only should basic data be recorded, but the forms should be considered an integral part of the analysis and kept as an important record of the history of treatment. Maintenance of accurate and usable records is not an end in itself, but it is an indispensable element of good laboratory work and good plant operation.

## BACTERIOLOGICAL EXAMINATIONS

As indicated previously the significant bacteria are the members of the coliform group and thus the examination of water is centered around the isolation and numeration of this group of bacteria in the water sample. However, the total number of miscellaneous bacteria in a definite volume of the water (usually 1 ml.)

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may also indicate the quality of the water and in particular the effectiveness of treatment processes such as filtration or disinfection

Thus frequently the bacteriological examinations are divided into two basic types—the total bacterial count or as it is usually designated, the standard plate count and the tests for the coliform group

### LABORATORY FACILITIES

It is essential for satisfactory work in the bacteriological examination of water that a suitable laboratory with all the required equipment in good working order be available. This laboratory should be reasonably isolated in order that the work may be conducted without danger of contamination from dust or other sources. An incubator preferably electrically heated that will maintain a constant and uniform temperature at 34° to 36°C must be provided and must be of ample size for the volume of work to be undertaken. In addition, there must be sterilizers for the sterilization of culture media glassware and other equipment required for these examinations.

Ample stocks of glassware—Petri plates, pipets and other items—must be maintained for immediate use. must be clean and sterile and kept in a sterile condition. A refrigerator is also an important item of equipment. An effective device for counting colonies under a magnification of approximately 3X is needed as well. For the preparation of culture media, dehydrated media obtained from reliable laboratory supply companies should be used and ample stocks should be maintained.

For accurate bacteriological work the laboratory and all equipment should be kept scrupulously clean and orderly.

### GENERAL LABORATORY EQUIPMENT

**Apparatus Incubators.** Incubators must maintain a uniform and constant temperature at all times in all areas. This can be accomplished by the use of a water-jacketed or anhydric type with thermostatically controlled low temperature electric heating units properly insulated and located in or adjacent to the walls or floor of the chamber and preferably equipped with mechanical means of circulating air.

Incubators should be provided with shelves so spaced as to assure uniformity of temperature throughout the chamber. The inside dimensions of the chamber should be adequate to accommodate without crowding 160 to 200 Petri plates or an equivalent mass of fermentation tubes. A 1 in. space should be provided between adjacent piles of plates and between walls and piles.

An accurate thermometer (checked against one certified by the National Bureau of Standards) with the bulb continuously immersed in liquid (glycerine water or mineral oil) should be maintained on each shelf within the incubator and daily readings of the temperatures recorded. In addition, it is desirable to maintain a maximum and minimum registering thermometer within the incubator on the middle shelf to record temperature variations over a 24 hr period. Temperature variations within the incubator when filled to maximum capacity should be determined at intervals. It is recommended that a recording thermometer be installed in every incubator whenever possible so that a permanent record of temperature variations within the incubating chamber may be maintained.

**Hot Air Sterilizing Ovens.** Hot air sterilizing ovens should be of sufficient size to prevent crowding of the interior constructed to give uniform and adequate

sterilizing temperatures, and equipped with suitable thermometers capable of registering accurately in the range  $160^{\circ}$  to  $180^{\circ}\text{C}$ . The use of a temperature-recording instrument is optional.

**Autoclaves.**—Autoclaves should be of sufficient size to prevent crowding of the interior; should be constructed to provide uniform temperatures within chambers (up to and including the sterilizing temperature of  $121^{\circ}\text{C}$ .); should be equipped with accurate thermometers with the bulb properly located on the exhaust line so as to register minimum temperature within the sterilizing chambers (temperature-recording instrument is optional); should have pressure gauges and properly adjusted safety valves connected directly with saturated steam power lines or directly to a suitable special steam generator; and should be capable of reaching the desired temperature within 30 min. In emergencies, where results have been demonstrated to be satisfactory, a pressure cooker may be substituted for an autoclave, provided that it is equipped with an efficient pressure gauge and with a thermometer whose bulb is 1 in. above the water level.

**Colony Counters.**—Standard apparatus, such as a Quebec colony counter, dark-field model preferred, or one providing equivalent magnification and visibility, should be used.

**pH Equipment.**—Electrometric pH meters or colorimeters, with standards, should be used for accurate determination of pH values of media.

**Balances.**—Balances providing a sensitivity of at least 2 g. at a load of 150 g. should be used, with appropriate weights. An analytical balance having a sensitivity of 1 mg. under a load of 10 g. should be used for weighing small quantities (less than 2 g.) of materials.

**Sample Bottles.**—A bottle of glass or other material resistant to the solvent action of water, capable of being sterilized, and of any suitable size and shape may be used for the bacterial examination. It should hold a sufficient volume of sample for all the required tests, should permit being properly washed, and should maintain the sample uncontaminated until the examinations are completed. Ground-glass stoppered bottles, preferably wide mouth, of resistant glass are recommended.

Metal or plastic screw cap closures may be used on sample bottles, provided that no volatile compounds are produced on sterilization and that they are equipped with liners that do not produce toxic or bacteriostatic compounds on sterilization.

The tops and necks of sample bottles with glass closures should be covered with metal foil, rubberized cloth, or heavy impermeable paper or milk bottle cover caps before sterilization.

## WASHING AND STERILIZING

All glassware should be thoroughly cleansed using a suitable detergent and hot water, and should be rinsed with hot water to remove all traces of residual washing compound.

Glassware, except when in metal containers, should be sterilized for not less than 60 min. at a temperature of  $170^{\circ}\text{C}$ ., unless it is known from recording thermometers that the oven temperatures are uniform, under which exceptional condition  $160^{\circ}\text{C}$ . may be used. Glassware in metal containers should be heated to a temperature of  $170^{\circ}\text{C}$ . for not less than 2 hr.

Sample bottles other than of plastic may be sterilized as above or in an autoclave at  $121^{\circ}\text{C}$ . for 30 min. Plastic bottles may be sterilized in an autoclave at  $121^{\circ}\text{C}$ . for not less than 10 min.



## CULTURE MEDIA

The preparation of the culture media required for each of the suggested technical procedures is given under each procedure. Further details regarding those media methods of preparation and specifications of the particular ingredients can be found in the latest edition of *Standard Methods for the Examination of Water and Waste Water*<sup>2</sup>. The use of commercially prepared dehydrated media is recommended in order to provide uniformity in these essential factors in the technical procedures. The directions for the preparation of the dehydrated materials as given by the manufacturer should be strictly followed in all details.

## TOTAL BACTERIAL COUNT—STANDARD PLATE COUNT

**Purpose of Test**—To provide an estimate of the total number of bacteria in a sample which will grow at 35°C in 24 hours and under the conditions of food supply and moisture provided in the accepted laboratory procedure.

**Sampling**—Samples must be collected in sterile glass stoppered clear glass bottles following the directions as given previously.

**Apparatus and Materials** Distilled Water

Harvard Trip Balance

Autoclave (or Pressure cooker autoclave with Fletcher solid flame burner)

Dehydrated Tryptone Glucose Extract Agar<sup>3</sup>

Oven or Hot Air Sterilizer to Operate at 170°C

Incubator—Equipped to maintain constant temperature between 34° and 36 C. in incubation chamber

Petri Plates—Glass with glass covers 90 mm diameter 15 mm deep

Pipets—Glass straight walled to deliver 1 ml

Erlenmeyer Flasks—125 ml Pyrex

Graduate—1000 ml graduated in 10 ml

Illuminated Colony Counter—Quebec Colony Counter

**Procedure** Preparation of Agar—1 Weigh 12 g of the dehydrated tryptone glucose extract agar or other agar media

2 Measure 500 ml of distilled water in a graduate

3 Pour 400 ml of the distilled water into a beaker and heat to boiling

4 Suspend the 12 g of agar in the remaining 100 ml of cold water

5 With constant stirring add the agar suspension to the 400 ml of boiling water continue stirring and boiling until the medium is completely dissolved

6 Pour equal amounts of the medium into each of ten 125 ml Erlenmeyer flasks

7 Close the Erlenmeyer flasks with cotton plugs

8 Sterilize in an autoclave for 15 min after the pressure has reached 15 pounds

9 Remove from autoclave as soon as the pressure returns to zero pounds the total time in the autoclave including heating sterilizing and cooling should not exceed 40 minutes

**Sterilization of Glassware**—1 Wrap Petri plates in groups of 4 in kraft paper or pack in metal cans

2 Wrap pipets in kraft paper or place in metal pipet can

3 Sterilize in oven by heating at 170°C for 1 hour

<sup>2</sup> The American Public Health Association Inc. 1790 Broadway New York N Y

<sup>3</sup> Other agar media—Plate count agar or Protein Hydrolysate agar—as given in *Standard Methods for the Examination of Water and Waste Water* may be used

Determination.—1. Melt the sterile agar by immersing the 125-ml. Erlenmeyer flask in boiling water.

2 Cool the melted agar to 45°C. and hold in a water bath at 43–45°C.

3. Shake sample violently in an up-and-down motion 25 times.

4 Aseptically, with a sterile pipet, transfer exactly 1 ml. or decimal aliquot of well shaken sample to a sterile Petri plate.

5. Add 10 ml. of melted agar medium cooled to 43°C.

6 Mix by rotating plate on surface of work table.

7. Allow medium to harden and place Petri plate in incubator maintained at 34–36°C.

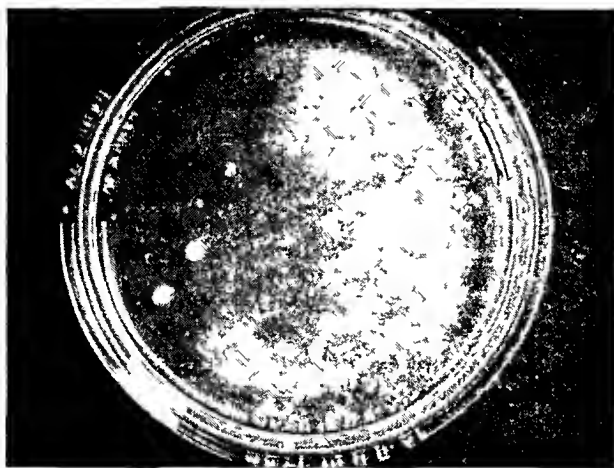


FIG. 49-1. Standard Plate Count Bacterial Colonies.

8. After 24 hours, count the number of colonies on or in the agar medium using an illuminated colony counter.

9 If the number of colonies present are too numerous to count, estimate the number by counting a fraction of the plate, such as one-quarter or one-tenth and multiply this count by the approximate factor.

Results.—Results are reported at 35°C.—24 hour agar plate count per ml. Express count to two significant figures only

*Interpretation.*—The standard plate count at 35°C indicates the number of microorganisms which develop best at this temperature, and since many of them are associated with animal life, the count is an additional indication of pollution. No definite standard can be set for the total count but usually it should be less than 500 per ml. Higher counts indicate possible contamination with surface drainage or with sewage. In filtered water high counts may indicate bacterial growths in filters, filtered water basin, or pipe lines.

## TEST FOR BACTERIA OF THE COLIFORM GROUP

### MULTIPLE TUBE DILUTION TECHNIC

*Purpose of Test.*—To estimate the number of bacteria of the coliform group present in a given volume of water as an index of the degree of pollution.

## 2510 WATER BACTERIOLOGICAL EXAMINATION

**Sampling**—Use the same sample collected for the total bacterial count (standard plate count)

**Apparatus**—In addition to that required for the standard plate count

**Fermentation Tubes**, for 10 ml volumes of sample culture tubes without lip  
175 x 22 mm

**Culture Tubes**—Without lip 75 x 10 mm for inner tubes

**Fermentation Tubes** for 1 ml volumes of sample culture tubes without lip  
150 x 18 mm

**Pipets** volumetric transfer 10 ml

**Baskets or Racks** for holding media

**Inoculating Loop** for transferring cultures

**Dehydrated Brilliant Green Lactose Bile Broth** 2%

**Procedure** **Preparation of Lactose Broth**—The medium after inoculation with the sample should contain 0.5% each of lactose and peptone. Thus in tubes to which 10 ml of water is to be added the medium must be made up to double strength

- 1 Weigh 13 g of dehydrated lactose broth
- 2 Measure 500 ml of distilled water in a graduate
- 3 Heat 400 ml of the distilled water to boiling
- 4 Suspend the weighed lactose broth in the remaining 100 ml of cold distilled water
- 5 With constant stirring add the suspension to the boiling water and dissolve completely
- 6 Into each of the large tubes (175 x 22 mm) insert one of the small tubes (75 x 10 mm) in an inverted position
- 7 Add 10 ml of medium to each tube
- 8 Close each tube with a cotton plug
- 9 Place tubes in basket and put in autoclave
- 10 Sterilize for 15 minutes after the pressure has reached 15 pounds
- 11 Remove from the autoclave as soon as the pressure has returned to zero  
The total time for heating, sterilizing and cooling should not exceed 40 minutes

**NOTE** In tubes to which 1 ml of sample is to be added normal strength medium is used for this purpose in Step 1 above weigh 6.5 g and in Step 6 use tubes sized 150 x 18 mm otherwise follow the same procedure

**Preparation of Brilliant Green Lactose Bile Broth**—The procedure is exactly the same as for the preparation of lactose broth except that 20 g of dehydrated medium are used for 500 ml of distilled water. Only single strength medium is prepared as no direct inoculations are made and only the 150 x 18 mm tubes & the inner tubes are used

**Sterilization of Glassware**—Use the same procedure as for the total bacterial count (standard plate count)

**Determination Presumptive Test**—1 In an aseptic manner inoculate each of five large fermentation tubes containing double strength lactose broth with 10 ml of sample

2 Inoculate 1 small fermentation tube containing lactose broth with 1 ml of sample

3 Inoculate 1 small fermentation tube containing lactose broth with 0.1 ml of sample

4. Place all fermentation tubes in incubator maintained at  $35^{\circ} \pm 1^{\circ}\text{C}$ .
5. At end of 24 hours observe if gas has formed in inner tube of each of the fermentation tubes.
6. Perform confirmatory test on all tubes in which gas has formed, and replace rest of the tubes in incubator.
7. At end of 48 hours observe if gas has formed in inner tube of each of the remaining lactose tubes.
8. Perform confirmatory test on all tubes in which gas has formed.

*Confirmatory Test.*—The production of gas in the lactose broth does not necessarily indicate the presence of bacteria of the coliform group because there may

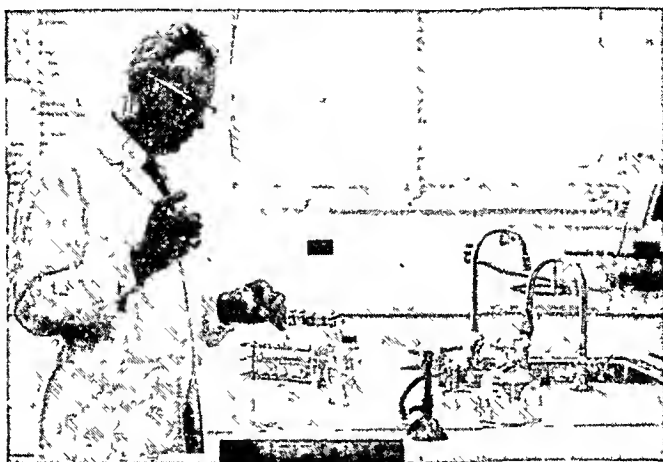


FIG. 49-2. Multiple Fermentation Tube Technic.

be other bacteria present which ferment lactose. If culture from those lactose broth tubes which show gas is transferred to brilliant green bile broth, the bacteria other than coliform organisms are inhibited by the brilliant green bile and any gas which is produced in these tubes can be assumed to indicate the presence of bacteria of the coliform group.

1. Select each fermentation tube showing gas at 24 or 48 hours (step 6 and 8 of presumptive test above) and transfer a loopful of broth to a fermentation tube containing brilliant green bile broth.
2. Place in incubator for 24 hours.
3. Examine for presence of gas; if gas is present the tube may be recorded as positive and discarded; if no gas is present it should be reincubated for another 24 hours and re-examined.
4. If gas is present at the end of the second 24 hours the tube may be considered positive; if no gas is present it is negative.

*Interpretation.*—Any lactose broth fermentation test showing gas formation after 24 or 48 hours incubation, confirmed by gas formation in the confirmatory medium after 24 or 48 hours, indicates the presence of bacteria of the coliform group in the corresponding volume of sample used. By using different volumes of sample, in multiples of 1 ml., it is possible to make a partial quantitative estimation of the

number of coliform bacteria in the samples. If the number of positive and negative tubes in each dilution is known, it is possible to calculate the probable number of organisms of this group in a given volume of water. This provides an index of pollution which is usually expressed as Most Probable Number (M P N) of Coliform Bacteria per 100 ml of Sample. This index represents that number of bacteria of this group which more frequently than any other number will give the observed results. The table may be used for determining M P N when five 10 ml, one 1 ml, and one 0.1 ml portions are used.

TABLE OF MOST PROBABLE NUMBER (M P N) FOR 100 ML SAMPLE  
USING INDICATED NUMBER OF VOLUMES AND PORTIONS

10 ml portions	1-ml portion	0.1 ml portion	M P N
-----	-	-	<2.2
+-----	-	-	2.2
++----	-	-	5.0
+++---	-	-	8.8
+++++-	-	-	15.0
++++++	-	-	38.0
++++++	+	-	240
++++++	+	+	2400 or >

The examination of volumes and portions other than those indicated above may be used and yield adequate data concerning water quality. If a different number of portions of another series of volumes of samples are inoculated in the multiple tube dilution technic for the detection and enumeration of coliform bacteria, the most probable number index corresponding to the bacteriological results can be obtained by use of other tables based upon the particular series of volumes and tubes used. These additional tables can be found in the latest edition of Standard Methods for the Examination of Water and Waste Water.

## TESTS FOR PRESENCE OF MEMBERS OF COLIFORM GROUP

### MEMBRANE FILTER TECHNIC

In this method a measured volume of water is filtered through a cellulose filter so prepared as to have many thousand tiny pores of uniform size. The bacteria too large to pass through the tiny pores are strained out and held on the surface of the filter. The filter pad is impregnated with a suitable culture medium which will stimulate the growth of bacteria of the coliform group while inhibiting the development of other types which may be present. After addition of the culture medium this filter is incubated at a temperature of 35°C, the optimum range for the growth of coliform bacteria. These organisms multiply, develop colonies on the medium and produce the waste products of their growth which react with indicator compounds contained in the medium. This reaction gives a red color to the colonies and a metallic sheen on their surface, both characteristic of coliform bacteria. The count of these colonies yields an estimate of the number of coliform bacteria in the volume of sample filtered.

The culture media at present proposed for use in the test yield results somewhat at variance with those obtained by the dilution tube procedure. With the

microfilter technic the coliform findings tend to be lower than the dilution tube results, which in turn may indicate a higher density of coliform bacteria than is actually present. Thus, if used for the bacteriological examination of water, the microfilter must be employed with full realization of the significance of the results. It does offer a useful means for the rapid evaluation of water quality and for routine control of water treatment.

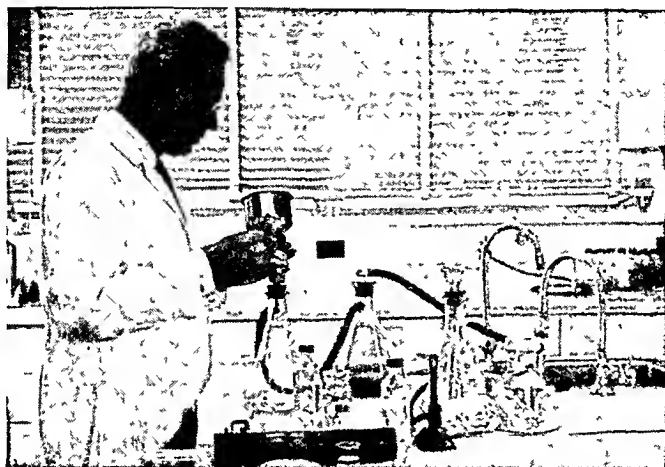


FIG. 49-3. Membrane Filter Technic.

The sample volume should be chosen on the basis of previous experience to produce from 20 to no more than 100 colonies on the medium. When volumes less than 30 ml. are selected, they should be diluted to at least 100 ml. with sterile water before filtration. Volumes from 100 ml. to 500 ml. are usually satisfactory for filtration.

The physical and chemical characteristics of water do not influence the results of the test except that turbidity and suspended matter will collect on the surface of the filter and interfere with colony formation and obscure the color and metallic sheen characteristic of coliform bacteria.

### STANDARD TEST

*Sampling.*—Samples should be collected in accordance with the directions given previously.

*Apparatus.* Glassware, in general the same as indicated for use in other bacteriological procedures.

*Culture Dishes.*—Culture dishes of the Petri plate type should be used. The bottom of the plate should be flat and should be 5 to 6 cm. in diameter so that the absorbent pad for nutrient will lie flat. The glass should be borosilicate or equivalent grade. Clean culture dishes may be wrapped singly or in convenient numbers, in metal foil or a suitable paper substitute, prior to sterilization.

Glass Petri plates are preferable for use in routine laboratory analyses. The optional containers described below are recommended for field use or under other conditions not favorable for cleaning, sterilization, and reuse:

*Disposable Plastic Dishes*, or their equivalent may be used. Sterilization should be accomplished by exposure of the opened culture dishes to ethyl alcohol ethylene oxide ultraviolet radiation or other appropriate chemical or physical agents. Choice of means of sterilization should be governed not only by convenience but also by actual tests demonstrating the effectiveness of such means of sterilization. The freedom of the culture containers from residual growth suppressive effects resulting from the methods of sterilization must be demonstrated. After sterilization and removal of the agent of sterilization the containers should be closed employing sterile techniques and stored in a dustproof container until used.

*Seamless Tin Ointment Boxes* 1 oz. with curled edge and 49 mm. inside diameter of top are acceptable subject to the above restrictions.

**Filtration Units**—The filter holding assembly should consist of a seamless funnel which fastens to a receptacle bearing a porous plate for support of the filter membrane. The parts should be so designed that the funnel unit can be attached to the receptacle by means of a convenient locking device. The construction should be such as to insure that the membrane filter will be securely held on the porous plate of the receptacle without mechanical damage and that all the fluid will pass through the membrane in the filtration of the sample. The filter holding assembly may be constructed of glass porcelain or any noncorrosive bacteriologically inert metal. It is recommended that the two parts of the assembly be wrapped separately in heavy wrapping paper for sterilization and storage until use.

For filtration the receptacle of the filter holding assembly is mounted in a 1 liter filtering flask with a side tube or other suitable device such that pressure differential can be drawn on the filter membrane. The filter flask should be connected by the side arm to an electric vacuum pump filter pump operating on water pressure hand aspirator or other means of securing a pressure differential.

**Filter Membranes**—Only those filter membranes may be employed which have been found by complete laboratory tests to provide full bacterial retention stability in use freedom from chemicals inimical to the growth and development of bacteria and satisfactory speed of filtration. They should preferably be grid marked. Several different brands of membrane filters meeting these specifications can be obtained from manufacturers and suppliers of laboratory equipment.

Filter membranes must be sterilized prior to use preferably by autoclave. The brown paper separators but not the absorbent paper pads should be removed from the packaged filters. The filters should be divided into groups of 10 to 12 or other convenient units and placed in 10 cm Petri plates or wrapped in heavy wrapping paper. The membranes are then autoclaved 10 min. at 121°C (15 psi). At the end of the sterilization period the steam is allowed to escape rapidly to minimize the accumulation of water of condensation on the filters. Suitable packaged sterile filters can be purchased.

**Absorbent Pads**—Absorbent pads for nutrients should be disks of filter paper or other material known to be free of agents that inhibit bacterial growth. They should be approximately 48 mm. in diameter and of such thickness that they will absorb from 1.8 to 2.2 ml. of nutrient. The pads should be wrapped in heavy wrapping paper or packaged in 10 cm Petri plates in convenient numbers for sterilization. Sterilization in an autoclave is recommended.

**Definition**—In the membrane filter procedure all organisms that produce a dark (purplish green) colony with a metallic sheen in  $20 \pm 2$  hr. of incubation are considered members of the coliform group. The sheen may appear in a small

central area or cover the entire colony. The "coliform group" as thus defined is not identical with, but is believed to be roughly equivalent in sanitary significance to, the "coliform group" as defined earlier. In the examination of waters of unknown quality, particularly those showing a high percentage of false presumptive tests, it will frequently be necessary to conduct parallel studies in order to determine the direct relationship between the results with the membrane filter technique and those with the dilution tube test for coliform bacteria in that supply.

Coliform organisms present in the water may fail to produce typical colonies. Therefore, when found in large numbers, atypical colonies should be identified by subculture study. It is also possible that noncoliform organisms may be encoun-

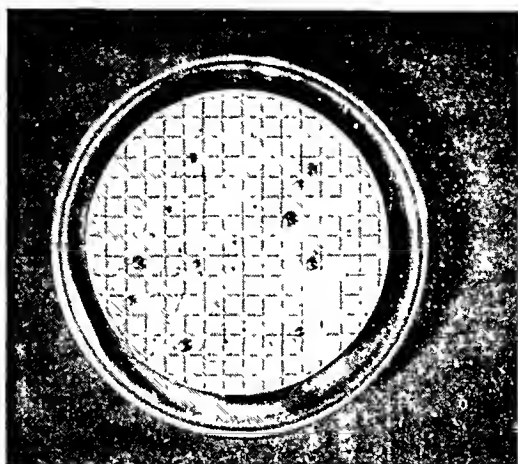


FIG. 49-4. Membrane Filter after Incubation Showing Typical Coliform Colonies.

tered in water which produce a colony typical of the coliform group. However, this happens so infrequently as to be of no significance.

**Procedure. Preparation of Culture Dishes.**—Place a sterile absorbent pad in each sterile culture dish. Pipet enough medium to saturate each pad, usually 1.8 to 2.2 ml.

**Selection of Appropriate Sample Volume.**—The size of the water sample will be governed by the expected bacterial density. An ideal quantity will result in between 20 and 80 coliform colonies, and not more than 200 colonies of all types, on the membrane. Large sample volumes from finished waters will be limited only by the presence of turbidity. Finished-water samples should be examined by filtering duplicate portions of a single volume or by one filtration for each of two aliquot volumes. All other water samples should be examined by one filtration for each of three aliquot volumes. Tentative suggestions for the examination of samples are as follows:

- a. Finished Water: Duplicate 100–500 ml. volumes.
- b. Well Water: Single filtrations of each portion examined—0.1, 1, and 10 ml.
- c. Polluted Water: Reduction in volumes in accordance with degree of pollution.

When less than 20 ml. is to be filtered, dilute with sterile buffered dilution water to a minimum volume of 30 ml. just before filtration.



**Filtration of Sample.**—Using sterile forceps, place a sterile filter membrane over the porous plate of the filter holding unit, grid side up. Carefully place the matched funnel unit over the receptacle and make it secure by means of the attachment device. The filtration procedure consists in passing the sample of water through the membrane under partial vacuum. After the sample has been filtered, rinse the funnel three times with 20–30 ml volumes of sterile buffered dilution water. Remove the membrane from the filter holding unit with sterile forceps, gently roll it, grid side up, onto the surface of an absorbent pad containing M Endo medium. Care must be used in placing the membrane to avoid entrapping air bubbles.

**Incubation.**—The membrane cultures are incubated  $20 \pm 2$  hr at  $35^{\circ}\text{C} \pm 0.5^{\circ}\text{C}$ , in an inverted position in the incubator with 100% humidity.

**Counting.**—All dark colonies having a metallic appearing surface luster are counted as coliform colonies. Make the counts with the aid of a low power microscope or other suitable optical device, using a light source above and approximately perpendicular to the plane of the filter membrane.

It should be noted that the characteristics of coliform colony types produced on modified Endo media with the membrane filter do not conform to those of coliform colonies developing on the Endo agar described in Sec 24c on p 497 of Standard Methods for the Examination of Water and Waste Water.

**Estimation of Coliform Density.**—The estimated coliform density of the sample is recorded in terms of coliforms per 100 ml sample. The computation can be made on the following basis:

$$\text{Coliform colonies 100 ml} = \frac{\text{Coliform colonies counted} \times 100}{\text{Sample filtered in ml}}$$

**Interpretation.**—The presence of 4 or more typical coliform organisms in 100 ml of water, as determined by the membrane filter technic indicates the presence of a significant amount of pollution in the water and thus unsatisfactory or unsafe sanitary quality. The presence of less than 4 coliform organisms per 100 ml will indicate acceptable sanitary quality.

## OTHER BACTERIAL TESTS OF WATER QUALITY AND OF POLLUTION

**Fecal Streptococci Types.**—Other types of bacteria, particularly certain streptococci, are present in the bodies of warm blooded animals and appear in their fecal discharges. These are designated as fecal streptococci and they are frequently advocated as an indicator of pollution in place of, or in addition to the coliform group. Fecal streptococci usually do not survive in water as long as do the coliform group. When found in significant numbers, these organisms suggest that the pollution is of recent origin and, thus, more significant or dangerous than that shown by the coliform group because of the possible presence of active pathogens which survive longer than the fecal streptococci, but which would probably be reduced in numbers by an unfavorable environment more rapidly and completely than the members of the coliform group. However the quality of the water would be equally unsatisfactory with recent or more remote pollution, since the important fact is that the water source had received sewage pollution.

The tentative technics for the detection and enumeration of fecal streptococci

in water may be found in the latest edition of Standard Methods for the Examination of Water and Waste Water.

## RESULTS OF BACTERIOLOGICAL EXAMINATION OF WATER

Bacteriological examinations of water are undertaken first to ascertain the quality of water and its suitability for domestic uses and second, to measure the efficiency of water treatment processes. The results of these examinations, therefore, must be interpreted to yield the information desired. For public water supplies, quality is generally defined in terms of the U.S.P.H.S. Drinking Water Standards (1962) which have been established for water supplies used in interstate carriers. These standards prescribe the minimum number of samples from a given supply for examination and further specify the maximum number of coliform organisms per 100 ml. allowable in an accepted and approved supply. These standards require in effect that in a series of 20 samples examined the coliform index shall be no greater than 1.0 per 100 ml., except that in a single sample, the index may be no greater than 9.0 per 100 ml. provided that this does not occur in two successive samples.

In the examination of a single sample, failure to detect coliform group microorganisms in any of the portions examined yields an index of less than 2.2 per 100 ml. and thus indicates a water of satisfactory and acceptable sanitary quality. An index higher than this, as 2.2 per 100 ml. or 5.0 per 100 ml. will indicate the presence of small but detectable amounts of pollution in the water, suggestive of questionable but possibly acceptable quality. Any index higher than 5.0 per 100 ml. can be considered presumptive evidence of unacceptable and even unsafe quality of the particular supply.

In the interpretation of the results of examination of a single sample or multiple samples from any type of supply—public, private or other—full knowledge of the history of the sample and the source, together with complete data relative to the construction of the supply, its operation and the location of potential sources of pollution is essential. Without such data the laboratory examinations are of little significance in evaluating the quality of the water.

The preceding discussion of bacteriological examination of water has been directed only to the problem of evaluation of the quality of water intended for beverage and domestic uses. The same technics can be and are used in the examination of water intended for other uses such as industrial operations, bathing and recreational purposes and also of water before treatment to improve its quality. Other standards of quality and other interpretations would of necessity be employed in the evaluation of quality for the specific use intended.

The procedures given above are essentially those as outlined in the latest edition of Standard Methods for the Examination of Water and Waste Water. Recommended technics for the bacteriological examination of water for purposes other than merely determination of sanitary quality are to be found in the above publication and this volume should be consulted for such technics when it is desired to examine water not from drinking water sources.

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## Chapter 50

# WATER: BIOLOGICAL EXAMINATION

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## INTRODUCTION

The quality of water, particularly as related to its palatability and acceptance for general household and domestic uses, is markedly affected by the presence and growth of minute microscopic animal and plant life within it.

These organisms are of many different types and forms. For convenience they can be grouped together and designated as plankton forms. The term "plankton" is used in a broad sense, to include microscopic and near microscopic free-floating organisms, and also minute attached forms usually found on the bottom surfaces of lakes and ponds. The term applies to the latter organisms only when they are detached and are found free-floating. Bacteria are excluded from the group, and are considered separately, both as to their significance and the technical procedures for their detection and enumeration.

Water undergoing storage in open areas is susceptible to the development of growths of these microorganisms, since they frequently find in such stored water an environment favorable for their life processes. In many such waters, particularly those polluted by community wastes, ample supplies of inorganic compounds, such as nitrates and phosphates, are present, and provide the essential food items demanded by the plankton. Unlike the bacteria, many species of plankton require sunshine for their activities and growth, and so develop on or near the surface of the stored water. Varieties that do not require or enjoy sunlight thrive in deeper portions of the reservoir, where the sunlight does not penetrate. Although many plankton forms need warm temperatures in their environment, others grow very well, and in some instances best, in cold water. Consequently, plankton growths are likely to appear on a seasonal basis, and may constitute a treatment problem throughout the year. One additional and striking feature of the fresh-water plankton, especially the plant portion or phytoplankton, is its cosmopolitanism. This means that organisms of this group can be found not only at all seasons of the year, but at most latitudes, and that problems relative to their control in reservoirs are practically universal.

Plankton in water undergoing storage markedly impair the quality of the water. The growths may at times appear as huge masses of floating scum, usually greenish

in color, unpleasant in appearance, and contributing to consumer rejection of the water as a source of domestic supply. When the plankton die and decompose, volatile compounds are liberated which, in turn, cause the water to have disagreeable and obnoxious tastes and odors, interfering seriously with its use for domestic purposes. Heavy growths of plankton also add to the amount of organic matter in the water, increase its color and turbidity, and present many problems in further treatment procedures.

The biologic examination of water is an important adjunct to techniques for the evaluation of water quality. The information obtained by such examination—usually designated as **microscopical examination** but more correctly as **biologic examination**—may be pertinent to several uses related to water quality and water treatment. These can be listed as follows: (a) to explain the cause of color and turbidity and the presence of objectionable odors and tastes in water, and to indicate possible methods for their prevention or removal, (b) to aid in the interpretation of the various chemical analyses, as, for example, in relating the presence of biologic forms to oxygen deficiency or supersaturation in natural waters, (c) to identify the source of a water that is mixing with another, (d) to explain the clogging of pipes and filters, and to aid in the design and operation of water works, (e) to indicate pollution by sewage or industrial wastes, (f) to indicate the progress of the self-purification of streams and other bodies of water, (g) to aid in explaining the mechanism of biologic sewage treatment methods or to serve as an index to the effectiveness of the treatment, (h) to aid in the study of the ecology of fish, shellfish, and other aquatic organisms, and to obtain information on food parasites and other factors affecting the well-being of these forms, (i) to determine whether or not ground water is contaminated by unfiltered surface water, (j) to determine optimum times for treatment of raw surface water with algicides and to check on the effectiveness of such treatment, (k) to determine, within the water plant, the effectiveness of various stages in the treatment of water.

Plankton organisms in general can live an independent life in water and can forage for their own food supplies.

Plankton forms of importance in water are algae, fungi, protozoa, rotifers, minute crustacea, and others. While they perform many duties related to the achievement of good water quality, they also present many problems in the necessary treatment procedures. In water, especially surface water that contains adequate concentrations of their required food items, the plankton will grow prolifically, and when the organisms finally die, the cells will decompose to release aromatic compounds and other decomposition products. These have characteristic and usually very potent odors which will then be present in the water and will impart to it distinctive and frequently objectionable tastes and odors. The type and intensity of the tastes and odors vary with each species and the rate of growth. Some actually may be intensified by chlorination. The removal of such tastes and odors from water, therefore, is an important function of water treatment, a function often difficult to carry out with the usual procedures. Preventing the growth of plankton in the original source is usually the most effective means to provide a satisfactory water supply free from the corresponding objectionable tastes and odors.

The population densities of plankton organisms in water are directly related to the various forms of nitrogen as determined in the chemical analysis and may often explain discrepancies and deviations in these determinations. With developing growths, concentrations of free ammonia and nitrate in the water will

decrease and organic nitrogen will increase. Decreasing growths will reverse these conditions.

One of the most important reasons for identifying and enumerating microscopic organisms is their connection with disagreeable, sometimes vile, tastes and odors in a water supply. The so-called littoral growths, which are attached to the banks or bottoms of reservoirs, and which frequently attract the greatest attention as a rule are not concerned. The trouble usually is caused by minute floating forms, which manufacture essential oils or perfumes like those of flowers. In exceedingly minute amounts, these substances produce pleasant aromatic, geranium, or grassy odors that become fishy, oily, pungent, or vile in larger amounts, or upon decay of the plant cells. So characteristic are the substances that the responsible genera may frequently be identified solely by the distinctive odor emanating from the water supply concerned.

Three principal groups of odors are distinguished: (1) aromatic, sometimes described as geranium or spicy, caused by Diatomaceae and some flagellates; (2) grassy, caused by Cyanophyceae and Chlorophyceae; and (3) fishy, caused by Chlorophyceae and a few Protozoa, and concentrated populations of others. Fishy odors often are produced by the same forms responsible for aromatic odors. This occurs when the populations of the latter are high.

The following table, as given by Whipple,<sup>1</sup> contains those organisms that have been observed at one time or another in sufficient quantity in a water supply to produce characteristic odors.

Some types, which are frequently the cause of impaired quality of water supplies, produce the specific type of odors as discussed below when present in the indicated numbers.

*Asterionella*, when present in 500 to 1000 cubic standard units per cubic centimeter, produces a slightly aromatic odor. At 1000 units, rarely less, the odor is distinctly similar to the odor of the geranium. The odor increases in intensity with increase in numbers until several thousand produce a fishy odor. The fishy odor is also produced when smaller quantities die.

*Tabellaria*, and similarly *Asterionella*, in very small amounts, produces a earthy odor (also produced by large amounts of *Synedra*), passing through the aromatic, geranium, and fishy stages with about the same relative quantities of organisms as *Asterionella*. At times the odor of *Tabellaria* has suggested illuminating gas, no other organisms being present. Complaints of fishy taste in the Catskill water supply for New York City have been occasioned by as little as 700 units of *Tabellaria*. This was the result of chlorination of the supply with liquid chlorine. The odor was not noticeable in the water above the chlorination plant but appeared first just below the plant. Chlorination killed the organisms, setting free the odorous principle.

*Anabaena* and *Aphanizomenon*, when present in 500 to 1000 units, produce a faintly grassy odor like freshly-cut grass or green corn. With larger numbers, the odor becomes pungent like nasturtium, or even onions. In large numbers, or when decaying, the odor is of a vile, pigpen character.

*Uroglenopsis* (*Uroglena*) produces an oily fishy taste and odor, first noticeable in probably 500 to 1000 units. In larger quantities it is very disagreeable. The flavor is that of cod-liver oil. Chlorine has an influence on this organism also.

<sup>1</sup> Fair and Whipple, *The Microscopy of Drinking Water*, John Wiley and Sons, Inc., New York, 1927. Table 50-1 embodies additions by the author.

TABLE 50-1

Group	Organism	Natural Odor
Aromatic odor	Diatomaceae	
	<i>Asterionella</i>	Aromatic, geranium, fishy
	<i>Cyclotella</i>	Faintly aromatic
	<i>Diatoma</i>	Faintly aromatic
	<i>Meridion</i>	Aromatic or spicy
	<i>Tabellaria</i>	Aromatic, geranium, fishy
Grassy odor	Protozoa	
	<i>Cryptomonas</i>	Candied violets
	<i>Mallomonas</i>	Aromatic, violets, fishy
	Chlorophyceae	
	<i>Dictyosphaerium</i>	Grassy
	Cyanophyceae	
	<i>Anabaena</i>	Moldy, grassy, green-corn, nasturtium
	<i>Aphanizomenon</i>	Grassy
	<i>Coelosphaerium</i>	Grassy, sweet
	<i>Microcystis</i> ( <i>Anacystis</i> )	Grassy, sweet
	<i>Cylindrospermum</i>	Grassy
	<i>Gloeotrichid</i>	Grassy
	<i>Rizularia</i>	Moldy, grassy
Fishy odor	Diatomaceae	
	<i>Asterionella</i>	Fishy in large numbers
	<i>Tabellaria</i>	Fishy in large numbers
	Chlorophyceae	
	<i>Dictyosphaerium</i>	In large numbers faintly fishy (also grassy)
	<i>Eudorina</i>	Faintly fishy
	<i>Pandorina</i>	Faintly fishy
	<i>Volvox</i>	Fishy
	Protozoa	
	<i>Bursaria</i>	Irish moss, salt marsh, fishy
	<i>Ceratium</i>	Fishy
	<i>Dinobryon</i>	Fishy, like rock weed
	<i>Glenodinium</i>	Fishy
	<i>Mallomonas</i>	Fishy in large numbers (also aromatic)
	<i>Peridinium</i>	Fishy, like clam shells
	<i>Synura</i>	Cucumber, fishy, musk-melon, bitter taste
	<i>Uroglenopsis</i> ( <i>Uroglena</i> )	Fishy and oily

*Synura* has caused trouble in as small an amount as 50 units. The odor is variously described as resembling cucumber, muskmelon, etc. It leaves a bitter aftertaste. Chlorine intensifies the trouble, so that only a few units are noticeable.

*Dictyosphaerium*, about 700 units, under influence of chlorine, has produced a grassy or pungent nasturtium odor.

Troublesome organisms occur chiefly in surface waters. Occasionally, well waters containing iron or manganese cause trouble from growths of *Crenothrix* and associated forms that clog pipes and cause an unsightly, turbid, discolored water. Well strainers become clogged preventing their proper yield of water.

Under ordinary circumstances, plankton organisms apparently do not affect the health. It is possible, however, that taste and odor may at times produce nausea or distaste for food, and that toxic blooms of algae may occur. Since it would take 12000 cubic standard units of *Asterionella* per cubic centimeter to add a milligram of solid matter to a glass of water, it is unlikely that harmful effects could be produced by water that satisfied the conditions associated with potability.

## SAMPLING FOR BIOLOGICAL EXAMINATIONS

### COLLECTION AND STORAGE OF WATER SAMPLES

**Equipment.**—Wide-mouthed, glass-stoppered, 2-l. glass bottles, and special types of sampling equipment.

The detailed specifications and directions for the use of these can be found in several texts, particularly in *Standard Methods for the Examination of Water and Waste Water*.<sup>2</sup>

**Sampling Points.**—Sampling points should be carefully selected to obtain representative samples. Special precautions should be taken to obtain a sample containing a typical dispersion of organisms, free from floating debris, mud, or extraneous material. The actual sites selected for collection should correspond as nearly as possible to those used in bacteriologic and chemical studies, in order to permit reasonable correlations.

**Collection of Samples.**—The plankton sample may be taken simultaneously with samples intended for biochemical or chemical analysis, and frequently, in the same sampler. If no sampler is available and a surface sample will be adequate, an ordinary glass bottle may be used. For this purpose a clean 2-l. bottle, not necessarily sterile, having a wide mouth and a glass stopper, is ideal. Smaller samples can be collected and, according to some workers, as little as 200 ml. may suffice. It is generally agreed, however, that a large sample is advantageous. In making the collection, the bottle, with stopper removed, is thrust as far as possible, mouth downward, into the water. It is then inverted and allowed to fill.

If the sample is to be examined while organisms are still alive—and this is often advisable in special studies where the greatest accuracy of identification is desired—it should be kept at its original temperature or iced to lower the temperature until an examination can be made. The bottle should not be placed in sunlight even on a cold day, and exhaustion of dissolved oxygen should be prevented by taking care not to fill the sample bottle completely. Such care is essential, as plankton organisms are very sensitive to environmental changes. One investigator, for example, reports that a rise of 10°C. in 30 min. is lethal to many

<sup>2</sup> *Standard Methods for the Examination of Water and Waste Water*, 11th Ed., American Public Health Association, 1960.



of the common plankton species and that frequently the lamp heat reaching the slide on the stage of a microscope is quickly fatal. The chilling that occurs when samples are iced appears to be relatively harmless.

**Preservation and Storage**—Unless the sample is to be examined fresh as indicated above it should be preserved immediately after collection by the addition of formalin. This is accomplished by adding 5 ml of commercial formalin<sup>3</sup> to each 100 ml of water. In routine sampling practice 40 ml of formalin is added to each liter of sample.

Since colors fade rapidly the preserved plankton sample must be stored in the dark. Under favorable conditions although carotenes and xanthophyll are said to break down chlorophyll retains its color rather well and it has been found that an expert can identify most organisms in a preserved sample even after several years of storage. For practical purposes a preserved sample has many advantages but it should be remembered that the plankton organisms in a preserved concentrate have been subjected to sudden immersion in a fluid that often produces severe contraction and distortion of body form. No ideal preservative has yet been found. The microscopist therefore must always be on the alert for misleading effects produced by the preservative. Comparison with an occasional live sample from the same source will aid the investigator to recognize forms that may be distorted in routine preserved samples.

## EXAMINATION OF THE SAMPLE

**Equipment Required** **Compound Binocular Microscope**—Providing magnification of at least 100. If possible an instrument with 2 additional objectives should be provided. These should give a magnification of 200 to 210 and 430 to 450 respectively. Such magnification is needed for the identification of many forms.

**Whipple Eyepiece Micrometer**—This should be equipped with fine graduations to indicate a standard unit at a magnification of 100. Since modern microscopes do not have an adjustable tube length this cannot be achieved exactly. A factor must be used.

**Standard Sedgwick Rafter Counting Cell**—Provided with extra cover slips.

**Stage Micrometer**—Used for calibration of the ocular micrometer.

**Sedgwick Rafter Funnels**—Three funnels are required with racks of wood or other material.

**Rubber Stoppers with Glass U Tube**—These shall fit small end of Sedgwick Rafter funnels.

**Silk Bolting Cloth Discs**—Adequate to fit over small end of rubber stoppers. The bolting cloth should be size No. 25 (200 meshes to linear inch or 40000 to the square inch).

**Standard Washed and Graded Sand**—Sand is required for use in the Sedgwick Rafter method of filtration. White sand passing a series No. 60 and retained by a No. 120 U. S. standard screen should be purchased ready for use.

**Glass Beakers** 50 ml—Six are required.

**Pipets**—Six 10 ml and six 1 ml pipets are needed.

**Graduated Cylinder**, 500 ml.

<sup>3</sup> Commercial formalin contains 37 to 42% formaldehyde. Since this type of formalin is usually acid having a pH of approximately 4 it may be desirable to render it neutral or basic. A slightly basic formalin is much to be preferred if specimens are kept for long periods of time. This adjustment can be provided by adding household borax hexamine or a concentrated ammonia solution to the formalin.

**Standard Reference Books.**—These will aid in identification of species. Standard Methods for the Examination of Water and Waste Water should be included.

**Concentration of the Sample—Sedgwick-Rafter Method.**—If organisms are numerous in the original sample, no concentration is necessary; in some instances, where a "water bloom" prevails, dilution of the water sample may actually be needed before enumeration can take place. There is no general agreement among workers in the field relative to the number of organisms needed per unit volume of sample to provide a basis for an accurate count, although it is hoped that current statistical research studies in this field may eventually provide a basis for agreement. For practical purposes, however, it is necessary to set some arbitrary limit. In doing so, it can be agreed that organisms are too numerous for an accurate count when they overlap one another in a standard counting cell. Conversely, organisms are too scarce when the average count per Whipple field, under standard procedure is less than 1.

It is suggested, therefore, that the ideal sample should contain a concentration of organisms that will produce a count of not less than 10 organisms for the entire square, when a Whipple micrometer and a standard counting cell are used. If this count is not attained, the sample should be concentrated. If other methods of counting are employed, the corresponding limit can be determined for the particular procedure.

Filtration should be carried out as soon as possible after collection of the sample. If the sample is kept cool, 3 or 4 hr. may safely intervene; but, for longer periods and at high summer temperatures, it is desirable to preserve the sample as directed above.

**Procedure.**—Prepare the Sedgwick-Rafter filter for use, first inserting the glass U-tube in the large end of the rubber stopper; then cover the moistened small end with a disc of bolting cloth, and place the whole firmly in the lower end of the funnel. The latter should be perfectly clean on the inside.

Pour sand into the funnel to form a layer  $\frac{1}{2}$  in. deep on top of the disc. Add 5 to 10 ml. of distilled water to wash down any sand on the walls of the funnel and to drive the air from the sand. As the distilled water filters through the sand, tilt the funnel from side to side to permit the air to escape.

Mix the sample well, but do not shake violently. Measure out 250 to 1000 ml., according to the density of the microscopic organisms in the sample, in a graduate, and pour slowly into the funnel, holding the latter in a slanting position and taking care to leave the sand undisturbed.

Allow the water to filter through the sand. Moderate suction may be used to hasten filtration. Wash down the side occasionally with the waste filtrate water from the sample. If living organisms are being concentrated, keep the temperature of the sample uniform during filtration to avoid the lethal effect of heat. After the water has reached the level of the outer arm of the U-tube, disconnect the suction, if employed; carefully remove the U-tube from the stopper to allow most of the remaining water to drain through the sand.

As soon as the sand has drained, transfer the funnel to a horizontal position, and remove the stopper slowly with a twisting movement; then raise the funnel to a vertical position inside a small beaker. The plug of sand usually falls into the beaker. Wash down the walls of the funnel with 5 to 20 ml. of waste filtrate water, the amount varying with the final concentration of sample desired. The water should be measured with a pipet, and is finally collected in the beaker containing

the sand and organisms. The container is then shaken gently to detach organisms from the sand grains.

Allow a moment for the coarse sand to settle then decant promptly into a beaker. A second washing with an additional 5 ml of water is usually necessary. If the mixing has been thorough any water remaining in the sand will have the same concentration of organisms as the decanted water of the second washing.

If the concentrated sample is to be preserved for future examination a 5% solution of formalin (5 ml of commercial formalin plus 95 ml of distilled water) may be used to wash down the funnel or the formalin may be added to the concentrate and the latter made up to a definite volume some multiple of 5 is convenient.

*Standardization of Microscope*—One eyepiece of the binocular microscope to be used in counting plankton is fitted with a glass disc (reticule) bearing parallel engraved equidistant lines for the measurement of objects or with an engraved subdivided square (Whipple disc) designed to accurately delimit a microscopic field. Before these ocular micrometers can be used they must be carefully calibrated in combination with each objective.

The ocular micrometers are calibrated by measuring an object of known dimensions thus determining the value of each subdivision by reference. A stage micrometer or glass slide on which an accurately ruled scale has been engraved is placed on the microscope stage and serves as the object of known dimensions.

The procedure consists of determining the number of intervals on the ocular micrometer required to cover one or several intervals on the scale of the stage micrometer. With the ocular and stage micrometers parallel and in part superimposed a line at one end of the eyepiece scale is selected and matched with a similar line of the stage micrometer scale. If the two scales are then carefully examined along their entire length it will be observed that the lines also correspond at another point.

Since the exact distance between lines on the stage micrometer is known the linear value of each ocular division can now be determined by reference. For example if the smallest interval on the stage micrometer is 0.01 mm and 25 of these 0.01 mm divisions are equal to 75 divisions on the ocular scale 1 ocular division =  $0.01 \text{ mm} \div 75 = 0.00033 \text{ mm}$   $33 \mu$ . When this ocular is used for measurement the result is a direct reading of the length of an object in microns. Thus an object covering 5 ocular divisions is  $165 \mu$  long.

When high power objectives are calibrated the stage micrometer lines are magnified to a point where they have appreciable width. As a result the calibration procedure must be modified by placing an ocular line alongside of rather than end to end with the stage micrometer lines. The ocular lines used for calibration should both lie on the same side of their stage micrometer counterparts.

Single observations will not suffice to establish a true calibration of ocular micrometers. The average of a large number of observations must be used. The data obtained will be more readily available if a graph is prepared in which the ocular scale dimensions are plotted against the linear distances they represent on the stage. By reference to this chart the length in microns of any given object examined may be determined quickly.

If the same eyepiece and objective are used and no change is made in the microscope tube length there will be no need to recalibrate an ocular micrometer.

The Whipple micrometer is usually calibrated by adjusting the tube length of the microscope at low power (16 mm objective) in such a way that the outer lines

of the square coincide exactly with the 0.0 mm. and 1.0 mm. lines on the stage micrometer. At higher powers, and where the tube length cannot be adjusted, the calibration is carried out in the same manner as for ocular measuring micrometers. Since the reading will not be exactly 1.0 mm. in the latter case, a factor must be used to convert plankton counts to the standard value.

**Selection of Aliquot Portion for Examination.**—The portion taken from a concentrated sample should be representative, and the examination should include a sufficient number of organisms to insure accuracy.

**Sedgwick-Rafter Cell Method.**—Shake the concentrated sample gently but in such a manner that complete mixing will occur. Place the cover glass obliquely across the cell. By means of a pipet, withdraw 1 ml. of material from the sample bottle before the motion of the sample induced by mixing has ceased. Introduce half at each open corner of the cell. When carefully done, this will cause the cover slip to rotate automatically into a position completely covering the cell. After a 4- to 5-min. settling period, the cell is ready for the enumeration procedure. During this interval most organisms settle toward the bottom and a few rise to the surface, coming to rest against the cover slip.

**Count of Organisms.**—The organisms are counted in terms of areal or volumetric standard units. The unit of measurement is a micron and an areal standard unit is defined as a square  $20\ \mu$  on the side or 400 square  $\mu$ . A volumetric standard unit would thus be a cube  $20\ \mu$  on a side. This method of recording microorganisms has been in use for many years. The Whipple eyepiece micrometer is constructed to cover a square 1 mm. on a side or exactly 1 square mm. This is then divided into 100 smaller squares, and 1 of these smaller squares is subdivided still further into 25 subdivisions. Each of the very smallest squares covers an area of 400 square microns, and is, hence, equivalent to an areal standard unit. In the process of counting it is customary to enumerate the organisms while simultaneously recording their size in terms of area or of volume. In this way the significance of the different types of organisms is recorded more effectively than by mere enumeration of individuals. This is at once evident if it is remembered that one large organism may prove more serious than several very small ones. It is relatively simple to estimate the average diameter or length and breadth of an individual organism for comparison with the smallest square of the Whipple micrometer that is equivalent to 1 standard unit. In this way, the size of the organisms may be determined and recorded. If the volume measurement is required, it can be determined by focusing the microscope from the top of the surface to the lowest surface (reading the vernier on the fine adjustment) to estimate the depth. The count of the individual organisms should be made in terms of either areal or volumetric standard units.

A differential count may be defined as the enumeration of some or all of the different kinds of plankton organisms, distinguishing them qualitatively. It involves identifying, counting, and recording the numbers of individuals of each kind. In contrast, the total count has been defined as an enumeration of all the plankton forms without any attempt to distinguish between different kinds.

In making a differential count, the contents of the cell should be examined under the microscope in three ways: first, the most abundant forms are counted by examining a number of standard fields; next, a strip extending the whole length of the cell is examined for organisms that are less numerous; and finally, the whole cell is examined for large forms and those very limited in number. In all cases, examine the full depth of the cell to include floating forms.

General rules or suggestions for counting, which are applicable to any of the three procedures listed, are as follows: (a) it is ordinarily impractical to count bacteria, (b) include in the count the remains of organisms living before the sample was preserved, but, if it is difficult to discriminate positively, do not count the doubtful specimens, (c) objects near the limit of vision of a given ocular and objective combination cannot be adequately counted. Examine them under higher powers, (d) detritus and objects other than plankton are recorded, if this information can be of any use in the final interpretation of results, e.g., counts of wood fibers derived from paper mills may be of value in pollution surveys (e) if a plankton organism lies on the boundary line of the field, count only that portion lying inside and record as a fraction. Another common system is to designate 2 adjacent sides of the field as counters and the opposing sides as 'noncounters', any organisms touching the 'counters' are counted, while those touching the opposite sides are ignored (f) the length of filamentous forms should be estimated and reported in units of a selected standard length, some workers report filaments in terms of 100  $\mu$  units (g) other forms having irregular colonies may be reported in terms of estimated units of volume, selecting arbitrarily a volume that approximates a medium size colony (h) except as indicated in (f) and (g), individual organisms should be reported whenever possible, unless colonial groups have a fairly constant number of cells. When a species of the latter type is reported in terms of colony units, it is well to indicate in the record the number of cells considered representative.

**Field Count**—The field count is made with the 16 mm objective and a 10 magnification ocular, equipped with a Whipple micrometer. When the distribution of organisms in the sample is uniform, and organisms are relatively abundant conditions are ideal for counting and relatively few fields need to be examined.

The exact number of fields that must be examined will vary considerably depending on the accuracy that is necessary, and the characteristics of the sample. Careful statistical work is currently being carried on to ascertain, on a mathematical basis, the exact number of fields that must be examined in any given sample to attain a preselected degree of accuracy.

For routine work it is recommended that, in samples that are adequately concentrated to provide at least 10 organisms per field, not less than 10 standard fields should be examined in making a plankton count. When special studies are being made, it may be necessary to increase the number of fields tenfold. Also when an 8 mm objective is substituted for the 16 mm objective, the number of fields examined must be increased from 10 to 40.

The fields selected should be taken at random, and should be well separated from one another. In order that certain parts of the cell may not be inadvertently avoided, some workers divide the area of the counting cell into 4 sectors by diagonal lines connecting opposite corners. Fields are then selected at random from each of the general areas so delimited.

In making a differential count, certain forms will be too scarce to appear in satisfactory numbers in each field examined, that is, less than 1 per field on the average. Such organisms must be counted by strip counts or survey counts.

**Strip Count**.—This count is made when a species is not abundant enough to be accurately enumerated by the Whipple field count. It is also suited to the enumeration of organisms that are too small to be identified or counted properly under the low magnification available in the basic field count method. The strip count is essentially the enumeration of a selected group of organisms as they occur

within an area represented by the full length of a Sedgwick-Rafter cell, 50 mm., and the width of a microscopic field, approximately 0.7 mm. The microscopic-field width generally used is that produced by a combination of a 10-magnification ocular and an 8-mm. objective. The exact width of this strip varies with individual lenses, and must be determined by reference to a stage micrometer. In a fully calibrated microscope, where the field diameter is known, it is a simple matter to convert strip counts into units that correspond with other methods.

In the actual count, enumeration is begun at one end of the cell, and all organisms that are to be recorded are counted as the slide is moved past the objective by the mechanical stage. Usually one trip is made along the long axis of the cell. In some instances it may be desirable to count several strips to obtain the accuracy desired.

**Survey Count.**—Large plankton forms, such as microcrustaceans and rotifers, which can be identified rather readily at low magnifications, and are less numerous than the smaller organisms, should be counted by the survey method. This involves enumeration of all organisms of this type that are present in an entire cell volume of 1 ml. Ideally, this count is made with a low-power stereoscopic microscope using its highest power. In routine work, however, most microscopists use the low-power objective, 16 mm., in combination with a 10-magnification ocular.

By means of the mechanical stage, the entire contents of the counting cell are moved past the objective for recognition and enumeration of the organisms that are being counted. In making this traverse, it is possible to include smaller plankton organisms if these have special significance and cannot be accurately counted by the other procedures.

If the total number of organisms is still too small for accurate reporting, several cells may be counted or the following supplementary procedure adopted: the entire sample is poured into a Petri plate, which is then examined under a stereoscopic microscope; guidelines or squares should be ruled on the Petri plate for the purpose of orientation.

The survey count is the method generally applied to silk net collections, although the field or strip count may also be used.

**Identification of Organisms.**—The plankton organisms found in the course of a biological examination of samples of water may be identified by carefully noting the size, configuration, and particularly, the color of the specific form seen in the microscope field. These observations can then be compared with the appearance of the different types as pictured in various texts and reference works on this subject, and the identity of a given organism thus can be determined with some assurance, to genus or to some more general group. A few of the types of plankton frequently encountered in surface waters are shown in Figs. 50-1 through 50-9. In making such comparisons, consideration must be given to potential malformations in the specimens isolated from the water, to variations produced by the point of view, and to other details that may be at some variance with the illustrations as found in the reference texts. Repeated examination of samples from a given source, and inspection at high magnification can do much to eliminate these difficulties.

Frequently, however, identification must be based on general and basic characteristics, and not on minute details of structure and color.

For routine examinations, specific identification of the plankton forms found may not be necessary, particularly if the group to which they belong can be ascer-

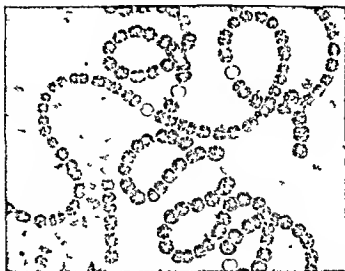


FIG 50 1 *Anabaena Circinalis*, Magnification Approximately 1000 (Rabenhorst 1852)

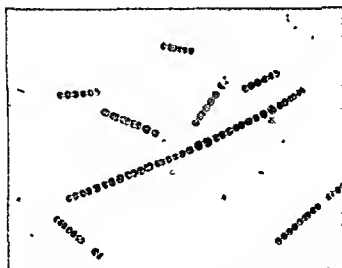


FIG 50 2 *Anabaena Flosaquae*, Magnification 300



FIG. 50-3. *Conferva*, *Synedra*, *Dinobryon*, Magnification 300.

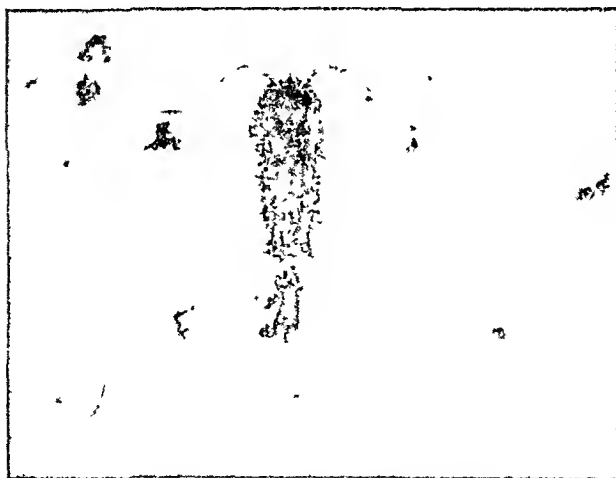


FIG. 50-4. *Cyclops*, Magnification 45.



tained, as Diatoms, Protozoa, etc. In many instances, all that will be required is an enumeration of the living organisms noted with reference to their general identity.

Preliminary identification of the forms found in a particular sample may be aided by considering some of the basic structural factors of a selected group of organisms commonly encountered in surface waters or in raw water supplies.

The genus *Asterionella* (little star), in its usual form, is readily recognized. Four to 8 arms connected at 1 end, and radiating from the attached ends suggest its name. If the inner, attached end is larger than the outer end of each arm the

species is *Asterionella formosa*, if of equal size it is *A. gracillima*. The arms are usually slender near the center in girdle view. The coloring matter appears as regularly spaced dots or dashes strung along the arm in a single row. There is another form of *Asterionella*, in which the arms attach at either end in a zig zag manner with occasionally 4 arms arranged in star fashion. This form may be confused with *Diatoma* or *Tabellaria*, but may be distinguished by the appearance of individual arms in valve view. *Diatoma* having very heavy cross striations and *Tabellaria* an oval swollen center.

It should be mentioned that Diatoms have 2 valves fitting together like clams, oysters or scallops, but different in that they overlap like the cover and bottom of a Petri plate or a pill box. The valve view is that of the top of the box, and the girdle view that of the edge. (Different authors use different terms. The above is according to Whipple.)

*Diatoma* in girdle view has straight sides and square ends, joining at the corners to form zig zag chains. The valve view is distinctive from *Asterionella* and from *Tabellaria*, it has heavy cross striations.

*Tabellaria* usually has wider arms than *Asterionella* or *Diatoma*, and 2 well defined parallel marks or lines extending from each end nearly to the middle. In some forms these are missing. The arms join in zig zag fashion with sometimes 3 or 4 in star shape. As mentioned before, the valve view is distinctive, being distinctly swollen or inflated at the center. There is also a distinctive short, chubby form with a similar swelling in the valve view.

*Fragilaria crotonensis* is a common and distinctive plankton form, it looks like an old fashioned double edged, fine toothed comb, when colonies are not too large. Some persons have referred to it as the "picket fence" *Fragilaria*. The needle like individuals of this diatom, tapered from the center to each end, are united at their centers, side by side, to form long ribbons in quiet water, shorter comb like lengths also occur if the ribbons are broken. These structures thus have 2 opposed comb like or serrated edges represented by the narrowed ends of each cell. Other species of *Fragilaria* do not have attenuated cell ends, and, therefore produce long ribbons of cells without serrations.

*Meridion*, like *Fragilaria*, has cells that are attached side by side, but being



FIG 505 *Daphnia*, Magnification 45



FIG 50 6 *Pediatrum Conferva*, Magnification 300.

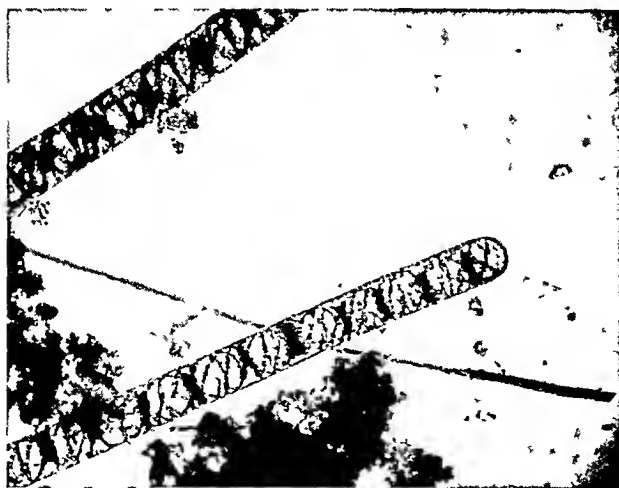


FIG 50-7. *Spirogyra*, Magnification 100.

wider at one end than the other they form a fan or disc like pattern instead of a ribbon. The valve view also is distinctive resembling a heavy baseball bat that is striated cross wise

*Gomphonema* also wedge shaped does not join in masses like *Meridion*. Cells are borne singly at the ends of a system of dichotomously branched gelatinous stalks from which planktonic forms have broken loose. In girdle view the cells are wider at 1 end than the other and hence wedge shaped. In valve view there is some variation but typically the shape is that of a mummy case.

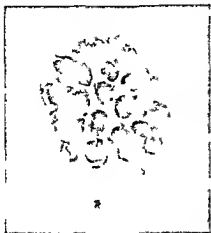


FIG 508 *Synura* Magnification 1100

*Synedra* is another very common component of the phytoplankton. The cells are usually narrow and many times longer than broad. Cells are solitary and free floating in most situations but frequently free floating colonies with cells radiating in all directions are encountered. Even within the same species there is a tremendous variation in length of individual cells.

Many forms once seen are very readily distinguished. *Stauroneis* appears as an elongated diamond with a cross marked from corner to corner. *Gyrosigma* with a double curve reminds one slightly of the letter S. *Navicula* is shaped as a little boat. *Melosira* has cylindrical cells joined end to end to form filaments containing considerable coloring matter. *Cyclotella* appears usually as small perfect circles or small Petri plates without contents whereas

*Stephanodiscus* is a larger Petri plate or pill box with conspicuous coloring matter and sometimes concentric markings visible on the circumference. On edge these pill boxes are seen as rectangles. *Stephanodiscus* also is typified by spines along the outer circumference top and bottom.

The coloring matter of the Diatoms may appear yellow to brown but in good light the chromatophores are yellow green. Sometimes there is not much suggestion of color.

The Chlorophyceae are strongly green in color. The common forms are readily distinguished and remembered from illustrations. *Dictyosphaerium* and *Dimorphococcus* are colonial forms in which the globose to reniform cells are joined by spider like threads to one another. The former has cells in 1 colony all of the same shape. The latter has colonies in which cells have 2 different shapes. *Pandorina* and *Eudorina* have spherical cells set in a jelly ball. The former with the coccus bodies grouped together very closely at the center. The latter with cells separated and spaced regularly near the surface. *Volvox* is a large revolving hollow ball having a surface dotted with spherical forms. It contains several conspicuous larger green cells. These are in reality young *Volvoxes*.

The Cyanophyceae or blue green algae contain a blue green coloring matter. *Anabaena* is a good example of this genus. It resembles a string of beads. *Nostoc* is very similar but differs in not having a gelatinous sheath. It differs from *Cylindrospermum* in that the latter has its heterocysts terminal with a large spore adjacent and that in the latter the filament is sometimes tapering.

*Aphanizomenon*, under high power, has a beaded appearance, and contains a very long oval spore, which is scarce. Heterocysts are also present and characteristic. Under the ordinary power *Aphanizomenon* appears as a pencil mark on drawing paper, and frequently the filaments appear in clumps that are large enough to be seen with the naked eye. In the field, these clumps resemble grass cuttings, and identification can be made on this basis.

*Oscillatoria* is a pale bluish filament of even color, usually with rounded ends, straight sides, and cross striations. In an unpreserved sample, it may often be seen to oscillate, or wave back and forth, and may even be observed to move slowly across the microscope field.

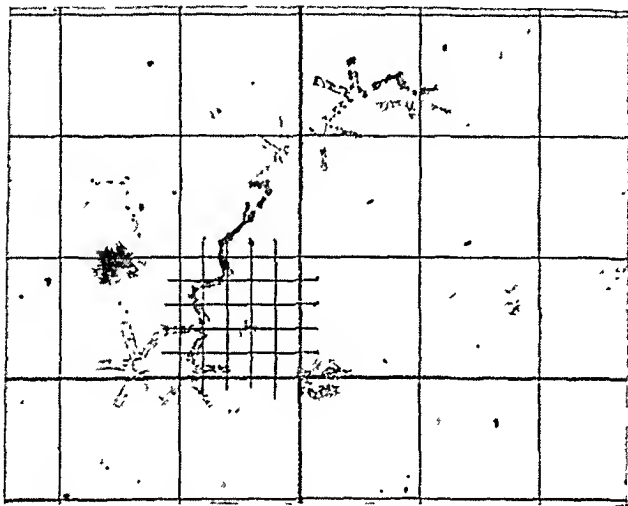


FIG. 50-9. *Tabellaria*, Magnification 200; Showing Whipple Eyepiece Micrometer.

Of the Schizomycetes, *Crenothrix* and *Leptothrix* are fairly common, and occur in well waters containing iron or manganese. They occur as dark brown masses due to discoloration with iron or manganese. If these are dissolved by acid, the oblong cells usually become visible, embedded in a gelatinous sheath, but not touching each other, and forming a filament. The yellow or brownish stalks of *Anthophysa*, a Protozoan, are sometimes mistaken for *Crenothrix* or *Leptothrix*, but the latter is usually branched like a "Y" and has longitudinal striations. The colonies of *Anthophysa* resemble *Synura*, but are colorless and generally smaller; if these colonies occur in a sample, one should check the filaments of iron bacteria very carefully.

The Protozoa are the lowest forms of animal life, unicellular in structure, though they may aggregate in colonies. *Dinobryon* is a form that contains chlorophyll and may be classified among the plants. Frequently when it occurs, only pencil-like outlines of the tiny cups or trumpet-like shells are visible; one set in another, to form branching aggregations. Spores of *Dinobryon* are sometimes mistaken for the Diatom, *Cyclotella*. *Glenodinium* and *Peridinium*, also carriers of chlorophyll, and therefore, plant-like, are oval with a groove across the center. The former is smaller and has a smoother outline than the latter. *Synura* is a small, moving, greenish-yellow to yellow ball of oval chlorophyll bearing organ-

isms joined concentrically and closely packed. *Uroglena* is a large jelly like hollow ball of minute chlorophyll containing animalcules, the latter embedded near the surface, similar in appearance to *Polyox*, previously mentioned, but lacking the large green cells (daughter colonies). *Uroglena*, when alive, rolls around slowly in the center of the liquid of a counting cell. Broken pieces have the shape of a piece of a rubber ball. It is just visible to the naked eye and is recognizable in the bottle.

*Rotifera*, *Crustacea*, *Tardigrada*, etc. (more complicated animal forms) are readily distinguished by their pictures in most instances. Many are visible to the naked eye. *Cyclops* may readily be recognized in the bottle by its shape and swift darting motion. It appears about the size of a pinhead, shaped somewhat like a tiny fish, but wider in proportion. *Bosmina* (little cow) and *Acarina* (little spider) both, have a peculiar, characteristic jerky motion. *Bosmina*, in a sense, reminds one of a tiny microscopic elephant.

**Calculation of Results. Record Forms**—Although it is difficult to design a bench sheet that will fit all situations in plankton counting, most workers find forms of this type very useful. Where repeated examinations are made of 1 sampling point or a series of similar sampling areas, a very satisfactory sheet can be prepared. Since there can be considerable latitude in the preparation of such forms, no exact specifications will be given.

Such forms should provide spaces for information on the identity and history of each sample. Included would be such items as the exact place and time of collection, the name of the collector, the time of arrival in the laboratory, the laboratory serial number, the date of examination, and the name of the examiner.

The manner of ruling the sheet may vary widely. In some instances 1 sheet will be ruled to facilitate entries when 10 fields are examined, the other will be set up for a procedure involving the examination of 5 fields, a procedure no longer recommended. Either form, however, may be adapted to counts where a larger number of fields is examined by making double entries in a square or by using 2 or more lines of squares in reporting the results. The form can be fitted to the requirements of the laboratory concerned, its chief function being to assure an immediate, accurate, and uniform recording of results.

**Reporting of Observations**—Reporting the number of organisms of each species is a straightforward procedure and requires much less time than a method that is based on the volume of each plankton species. In many instances, a simple count of this kind is entirely adequate for the practical problems involved, and may be used without modification. In other instances, where a fairly uniform plankton prevails and the same locality is examined repeatedly, the direct count can be converted into volume units by applying factors. For example, each species may be assigned a volumetric factor that for practical purposes, represents the average volume of any organism within the group. By applying this factor to the numerical count, the final report can be given in terms of volume. If desired, this figure can then be converted to its equivalent in cubic standard units. Some workers have stated that cubic standard units is a poor way to give volumetric reports and prefer to report their counts of living cellular matter as parts per million or milligrams per liter. In the latter procedure, the specific gravity of the organisms must be known. Ordinarily the practical worker assumes this value is 1.0, the same as that of water, and proceeds accordingly to report the plankton organisms in terms of milligrams per liter.

When colonial or filamentous forms are counted, they should be reported in terms

of standardized units. *Melosira* or *Oscillatoria*, for example, may be reported as units or fractions of units, 100  $\mu$  in length. In some colonial forms, the number of cells may be enumerated; more often it is desirable to report the number of colonies. In the latter procedure, especially where colony size may vary considerably, the volume of each colony should be estimated by reference to the Whipple micrometer guide lines, while the count is being made. The report can then be rendered in terms of an equivalent number of standardized medium-size colonies. The size of colony chosen as a standard may be arbitrary but should fall near the median. Such a procedure facilitates comparison of samples and, if desired, provides an easy basis for converting a numerical count into a volumetric equivalent.

In enumerating the organisms, the field count is usually made first, counting all organisms that lie within the limits determined by the Whipple disc. This count is carried out at a low power, with the 16-mm. objective and 10 magnification oculars.

It is followed by the strip count and survey count, which include organisms too scarce for accurate counting by the random field technique.

In recording the count, a bench sheet is very useful; the results are simply entered in their proper columns as the enumeration is carried out, and are then ready for summation. Certain modifications in the use of a form may be made to fit the situation at the time a count is made. When standard lengths of filaments and standard-size colonies are reported, suitable entries are conveniently made within parentheses following the name of the organism.

**Sedgwick-Rafter Cell Count—Cubic Standard Units.**—The following calculation is an example of the procedure followed when reporting in terms of cubic standard units. (Results may also be reported in terms of the number of organisms per unit volume of sample by a slight change in procedure.)

Record the total number of organisms, of standard units, or of both, found by examination of the 10 fields, or by mechanical-stage traverses.

Convert into terms of volumetric standard units the totals recorded for each species. This computation is not necessary where the bulk of a species has been estimated, whenever seen, in terms of volumetric standard units.

As each value of volumetric units is obtained, convert it into volumetric standard units per milliliter of original unconcentrated sample. The latter value is obtained by multiplying the volumetric units by suitable factors secured in the following way:

$$\text{factor} = \frac{\text{number of fields in 1-ml. counting cell 1 mm. deep}}{\text{number of fields counted}} \times \frac{\text{milliliters of concentrate}}{\text{milliliters of water in original sample}}$$

If, for example, there are 1000 fields in the counting cell, 10 fields are counted in the field count, 250 ml. of water are filtered, 15 ml. is the volume of the concentrate, and the cell holds 1 ml. and is 1 mm. deep, the formula becomes:

$$\text{field count factor or multiplier} = \frac{1000}{10} \times \frac{15}{250} = 6$$

In the survey, the entire cell is examined. If the conditions are the same as those above, 1000 fields are covered and the formula becomes:

$$\text{survey factor} = \frac{1000}{1000} \times \frac{15}{250} = 0.06$$

Multiplication of the results of the field count and survey by the respective factors gives the approximate actual volume of each organism in 1 ml of water. This can be converted into cubic standard units per liter by multiplying by 1000.

Record the volumetric standard units per milliliter of sample for each species observed in the survey and field count. Total the items in each column then add the 2 sums to obtain the final result which is expressed as total volumetric standard units or organisms per milliliter of sample. The volume of amorphous matter may be computed and recorded in similar fashion. To keep a record of the number of organisms use 2 additional columns subheaded Survey and Total Count respectively but with the main heading Number of Organisms.

**Number of Organisms**—The following calculation is used when reporting in terms of number of organisms per unit volume. (Results may also be reported in terms of cubic standard units by a slight change in procedure.)

The calculation is designed to give the number of organisms per liter rather than per milliliter as in the above example.

Record the field count total. Since it is recommended that 10 fields be examined this is the total number of organisms found in 10 fields.

Calculate the factors needed to convert the survey count, strip count and field count into number of organisms per liter of original unconcentrated sample. This can be converted into number per 100 liters by multiplying by 100 or into number per milliliter by dividing by 1000.

**Survey Count** The entire area of a Sedgwick Rafter counting cell or of several cells is examined. If the contents of 1 cell are examined and counted then

$$\text{factor} = \frac{\text{milliliters of concentrate} \times 1000}{\text{milliliters of original sample}}$$

**Strip Count**—One or several strips may be examined. If 1 strip is used then

$$\text{factor} = \frac{\text{area of cell}}{\text{area of strip examined}} \times \frac{\text{milliliters of concentrate}}{\text{milliliters of original sample}} \times 1000$$

**Field Count**—The total number of organisms in 10 fields is multiplied by a factor obtained as follows

$$\text{factor} = \frac{\text{number of fields in counting cell}}{\text{number of fields counted}} \times \frac{\text{milliliters of concentrate}}{\text{milliliters of original sample}} \times 1000$$

**Interpretation of Results**—If 300 or more cubic standard units of living organisms are found the water should be treated with copper sulfate to prevent possible trouble with taste and odor or interference with subsequent treatment procedures such as coagulation and filtration. From 100 to 300 cubic standard units indicates active growth of microorganisms. More than 500 cubic standard units indicates a serious condition. One thousand cubic standard units or more of amorphous matter indicate probable heavy growth of organisms that have died and disintegrated. The presence of a single individual of certain types of organisms such as *Synura* is an indication of potential taste and odor difficulties and in some situations may indicate the need for treating the water promptly with copper sulfate.

## CONTROL OF GROWTHS OF PLANKTON IN WATER

When storage reservoirs are subject to heavy seasonal growths of plankton and similar microorganisms, they should be given specialized treatment to eliminate such growths before they reach a magnitude that will impair the quality of the water. Although the elimination from reservoirs of drainage from swampy areas and of pollution may reduce growths, usually some more definite treatment is required. An effective procedure is the application to the reservoir of copper sulfate, which has a specific toxic action toward most of the plankton forms. The dosage of copper sulfate required is small, but varies with the species to be destroyed and with the chemical characteristics of the water. In the hard waters of the middle west, larger dosages must be used than in the soft water areas of the eastern United States. The dosage generally used is between 0.1 and 2.0 p. p. m. The copper sulfate is added in solid form. The solid dissolves in the water and destroys the living cells, and the copper is precipitated as copper carbonate. This precipitate then settles to the bottom of the reservoir and exerts little or no further action.

The growth of most plankton forms is at the surface or in the upper 20 ft. of depth. Thus, it is general practice to add only sufficient copper sulfate to yield the required dosage in the upper 20 ft. of water. In order to compute the amount of chemical required, and plan for its effective use, the area and profile of the storage reservoir must be known. Since 3 acre-feet of water is 1.0 million gal., computation of the amount of copper sulfate required is simple. The limiting dosages of copper sulfate as affecting fish life are given in Table 50-2.

TABLE 50-2. LIMITING DOSAGE OF COPPER SULFATE FOR FISH LIFE

Fish	Parts per Million	Pounds per Million Gallons (Approximate)
Trout.....	0.14	1.2
Carp.....	0.33	2.8
Suckers.....	0.33	2.8
Catfish.....	0.40	3.5
Pickrel.....	0.40	3.5
Goldfish.....	0.50	4.2
Perch.....	0.67	5.5
Sunfish.....	1.33	11.1
Black Bass.....	2.00	16.6

*Effects on Fish Life.*—In treating water with copper sulfate over-treatment must be avoided as this chemical is toxic to fish life, and excessive doses, particularly if concentrated in a local spot, will rapidly destroy fish in that area.



TABLE 50-3 CHEMICALS REQUIRED FOR TREATMENT OF DIFFERENT GENERA

Organisms	Odor	CuSO <sub>4</sub> , Parts per Million	CuSO <sub>4</sub> , Pounds per Mil Gals	Chlorine P p m.
<b>DIATOMACEAE</b>				
<i>Asterionella</i> ‡	Aromatic, geranium, fishy	0.12 *-0.20 *	1.0-1.7	0.5 *-1.0 *
<i>Cyclotella</i> †‡	Faintly aromatic	—	—	1.0
<i>Diatoma</i> †	Faintly aromatic	—	—	—
<i>Fragilaria</i> †		0.25	2.1	—
<i>Melosira</i> †‡§		0.2	1.7	2.0
<i>Meridion</i>	Aromatic	—	—	—
<i>Navicula</i> †		0.07	0.6	—
<i>Nitzschia</i> §		0.50	4.2	—
<i>Synedra</i> †‡	Earthy	0.36 *-0.50 *	3.0-4.2	1.0
<i>Stephanodiscus</i>		0.33	2.8	—
<i>Tabellaria</i> †	Aromatic, geranium, fishy	0.12 *-0.50 *	1.0-4.2	0.5 *-1.0
<b>CHLOROPHYCEAE</b>				
<i>Cladophora</i> †		0.50	4.2	—
<i>Closterium</i>		0.17	1.4	—
<i>Coelastrum</i> †		0.05-0.33	0.4-2.8	—
<i>Conferia</i> †		0.25	2.1	—
<i>Desmidiium</i>		2.00	16.6	—
<i>Dictyosphaerium</i> ‡	Grassy nasturtium fishy	—	—	0.5 *-1.0
<i>Draparnaldia</i>		0.33	2.8	—
<i>Eudorina</i>	Faintly fishy	2.0-10.10	16.6-83.0	—
<i>Entomophora</i>		0.50	4.2	—
<i>Gloeocystis</i>	Offensive	—	—	—
<i>Hydrodictyon</i>	Very offensive	0.10	0.8	—
<i>Microspora</i>		0.40	3.3	—
<i>Palmella</i>		2.00	16.6	—
<i>Pandorina</i>	Faintly fishy	2.0-10.00	16.6-83.0	1.0
<i>Protococcus</i>		—	—	—
<i>Raphidium</i>		1.00	8.3	—
<i>Scenedesmus</i>		1.00 *	8.3	—
<i>Spirogyra</i> †		0.12	1.0	0.7-1.5
<i>Staurastrum</i>	Grassy	1.50	12.5	—
<i>Tetrastrum</i>		—	—	1.0
<i>Ulothrix</i>		0.20 *	1.7	—
<i>Volvox</i> †	Fishy	0.25	2.1	0.3 *-1.0
<i>Zygnema</i>		0.50	4.2	—
<b>CYANOPHYCEAE</b>				
<i>Anabaena</i> †	Moldy, grassy, vile	0.12 *-0.48	1.0-4.0	0.5 *-1.0
<i>Aphanizomenon</i> ‡	Moldy, grassy, vile	0.12 *-0.50 *	1.0-4.2	0.5 *-1.0 *
<i>Clathrocystis</i>	Sweet grassy, vile	0.12 *-0.25 *	1.0-2.1	0.5 *-1.0
<i>Coelosphaerium</i> ‡	Sweet grassy	0.20 *-0.33	1.7-2.8	0.5 *-1.0
<i>Cylindrospermum</i>	Grassy	0.12	1.0	—
<i>Microcystis</i>		0.20	1.7	—
<i>Oscillaria</i> †		0.20-0.50 *	1.7-4.2	1.1
<i>Rivularia</i>	Moldy, grassy	—	—	—

The organisms where odors are expressed have been in sufficient quantity at one time or another to cause the characteristic odor

\* Dosage successful in New York City's supplies.

† These organisms have caused trouble other than odor

‡ These organisms have been affected by chlorine producing characteristic odor and in many cases controlled by dosage ranging from 0.3 to 3 p p m. depending largely on amount of organisms

§ Controlled by excess caustic lime, 5 p p m. in the case of the diatoms

NOTE — Range of dosage largely due to temperature

Methods for treating bodies of water for destruction of biological life can be found in many standard reference works on water supply treatment. To avoid difficulties these procedures should be followed in detail.

The recommended dosages in parts per million and pounds per million gallons of copper sulfate to be added to a water source for destruction of the various types of plankton organisms are given in Table 50-3.

### SUMMARY

The procedure for the biological examination of water given in detail in Standard Methods for the Examination of Water and Waste Water, is the one generally recognized and used. Modified technics have been proposed and, in many instances, may be superior to the standard Sedgwick-Rafter Method. Many methods for the collection of samples under special conditions, and employing various kinds of instruments for the purpose, are often recommended. The specialized details of these procedures for examination and for collection of samples can be found in the work cited above, as well as in other reference texts related to aquatic biology.

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